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# PROPERTIES OF NONAQUEOUS ELECTROLYTES

## FOURTH QUARTERLY REPORT

(20 March 1967 to 19 June 1967)

By

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Prepared For

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A Division of North American Aviation, Inc.  
Canoga Park, California



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#### FOREWORD

This report was prepared under G.O. 8852 in compliance with Article VI and Paragraph B of Contract NAS3-8521 for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio. The work was conducted in the Chemical and Material Sciences Department of Rocketdyne's Research Division, during the period 20 March 1967 through 19 June 1967.

#### ABSTRACT

Studies of aprotic electrolytes based on three solvents, propylene carbonate, dimethyl formamide and acetonitrile, were continued. Only characterized components were used to prepare the electrolyte solutions.

Structural studies of electrolytes containing tetramethylammonium hexafluorophosphate, lithium perchlorate, cupric chloride, and aluminum chloride with or without lithium chloride added were performed by nuclear magnetic resonance.

The physical property studies included measurements of viscosities, solubilities, conductances, and transference numbers of a number of electrolytes.



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## SUMMARY

Distilled solvent batches were analyzed by vapor phase chromatography on a routine basis. A new Porapak Q column was prepared which allowed better separation of water and acetonitrile (AN).

Spark source mass spectroscopic data for  $\text{LiClO}_4$  and  $\text{CuF}_2$  are given. The latter proved to be of unsatisfactory quality, and a synthesis of pure  $\text{CuF}_2$  will be attempted.

It was confirmed by additional nuclear magnetic resonance (NMR) evidence that tetramethylammonium hexafluorophosphate ( $\text{TMA} \cdot \text{PF}_6$ ) forms a  $\text{PF}_6^-$  species in dimethyl formamide (DMF) and that  $\text{LiClO}_4$  produces  $\text{ClO}_4^-$  ions in propylene carbonate (PC). Two copper species were found when  $\text{CuCl}_2$  was dissolved in dimethyl formamide, a paramagnetic species coordinating DMF molecules and a nonparamagnetic species. Two inequivalent aluminum atom environments are present in  $\text{AlCl}_3/\text{PC}$ . Both show narrow  $\text{Al}^{27}$  lines indicating tetrahedral or octahedral symmetry. Addition of  $\text{LiCl}$  to this  $\text{AlCl}_3$  solution caused one species to disappear. Similar results were obtained in acetonitrile.

Viscosities were measured for 1M  $\text{LiClO}_4$  solutions. The solubilities of  $\text{LiClO}_4$  and  $\text{TMA} \cdot \text{PF}_6$  were measured in PC and DMF with and/or without the addition of 1000 ppm water. The solubility of  $\text{CuCl}_2$  was determined in several electrolytes. A significant increase in solubility upon addition of 1000 ppm water was found only in cases of low solubility. Conductances were measured for various electrolytes, mainly  $\text{LiClO}_4$  and  $\text{LiBr}$  solutions. Transference experiments were made with electrolytes containing  $\text{LiClO}_4$  or  $\text{LiCl}$ , with  $\text{AlCl}_3$  and  $\text{CuCl}_2$  added in certain tests.





## DESCRIPTION OF PROGRESS

## PREPARATION OF ELECTROLYTES

Purification of Solvents

Solvents were purified by distillation and analyzed as described previously (Ref. 1 through 3). Summaries of both the distillation conditions and the analytical procedure normally applied were presented in Ref. 3. Table 1 lists the solvent batches used during the report period.

TABLE 1

## CHARACTERIZATION OF DISTILLED SOLVENT BATCHES

Solvent Code	H <sub>2</sub> O Content, ppm	Organics, ppm
PC #2-2	55	20
PC #2-3	25	None
PC #2-4	20	15
PC #2-5	20	35
PC #2-6	35	None
PC #2-7	20	35
PC #2-8	40	65 + 55 (two impurities)
PC #2-9	20	20
DMF #1-2	20	140
DMF #3-2	40	None
DMF #4-2	100	None
DMF #3-3	45	35
DMF #3-4	70	None
DMF #3-5	65	None
AN #1-2	40	None
AN #3-1	50	None
AN #3-2	80	None



### Analysis of $\text{LiClO}_4$ and $\text{CuF}_2$

Two solutes were analyzed by spark source mass spectrometry. The results obtained for lithium perchlorate ( $\text{LiClO}_4$  #2, 99.9 percent, Atomergic Chemetals Co.) are listed in Table 2 and the results for cupric fluoride ( $\text{CuF}_2$  #2, special quality, Ozark-Mahoning Company) in Table 3. These analyses were performed at the Bell and Howell Research Center, Pasadena, California. Results obtained by emission spectroscopy were reported previously (Ref. 2) and are added in Tables 2 and 3 for comparison purposes. Generally, the agreement between the two methods is good; an exception is the determination of Sn in  $\text{CuF}_2$ .

As in previous analyses (Ref. 2), no analyses for tantalum and gold were made. Elements not listed were not detected and have concentrations less than 10 ppm (atomic), with the exception of those which could not be determined because of interference by background lines. These were Mg, P, S, V, Cr, and Nb in the case of lithium perchlorate, and Si, Br, Cs, and Ba in the case of cupric fluoride.

The samples were not prepared for analysis under entirely anhydrous conditions (Ref. 2); therefore, the reported oxygen and hydrogen contents are upper limits, and the true values are probably much lower. Because the oxygen content of  $\text{CuF}_2$  is not balanced with the hydrogen content,  $\text{CuF}_2$  appears to contain some oxide.

Lithium perchlorate,  $\text{LiClO}_4$  #2, showed only one impurity element at a concentration above 100 ppm. It is not conceivable that this impurity (Na, 260 ppm per weight) will affect the measurements significantly. A spot test analysis for chloride revealed a  $\text{Cl}^-$  content below 20 ppm.  $\text{LiClO}_4$  #2 is being used after drying under vacuum at elevated temperature.



TABLE 2

IMPURITY CONCENTRATIONS IN  $\text{LiClO}_4$  #2 DETERMINED BY SPARK  
SOURCE MASS SPECTROMETRY AND EMISSION SPECTROSCOPY

Impurity	Spark Source Mass Spectrometry			Emission Spectroscopy
	Detection Limit, ppm atomic	Content, ppm atomic	Content, ppm per weight	Content, ppm per weight
H	3.0	500.0	28	
B	1.0	20.0	12	
C	1.0	20.0	14	
N	1.0	6.5	5.1	
F	2.0	23.0*	25*	
Na	0.3	200.0	260	
Al	0.5	1.0	1.5	
Si	1.0	23.0	36	10
K	0.3	16.0	35	
Ca	0.7	5.9	13	17
Cu	2.0	12.0*	43*	4
Zn	2.0	3.0	11	
As	1.0	21.0	89	
I	2.0	3.0	21	
Mg				3
Fe				2
Sn				4
Pb				16

\*May be due to residuals in the mass spectrometer



TABLE 3

IMPURITY CONCENTRATIONS IN  $\text{CuF}_2$  #2 DETERMINED BY SPARK  
SOURCE MASS SPECTROMETRY AND EMISSION SPECTROSCOPY

Impurity	Spark Source Mass Spectrometry			Emission Spectroscopy
	Detection Limit, ppm atomic	Content ppm atomic	Content, ppm per weight	Content, ppm per weight
H	3.0	910.0	27	
Li	0.3	0.5	0.1	
B	1.0	32.0	10.2	
C	1.0	320.0	114	
N	1.0	75.0	31	
O	1.0	2600.0	1230	
Na	0.3	300.0	204	
Mg	0.7	58.0	42	35
Al	0.5	130.0	104	170
P	1.0	12.0	11	
S	5.0	360.0	340	
Cl	2.0	250.0	260	
K	0.3	22.0	25	
Ca	0.7	18.0	21	86
Ti	7.0	N.D.	< 10	
V	1.0	30.0	45	
Cr	1.0	8.5	13	5
Mn	1.0	7.2	12	23
Fe	2.0	740.0	1200	1100
Ni	5.0	430.0	730	970
Zn	5.0	130.0*	250*	
Ga	0.7	1.5	2.7	
As	5.0	N.D.	< 11	
Ag	0.7	8.2	26	6
Cd	5.0	21.0	70	
Sb	1.0	1300.0	4000	400
Te	5.0	N.D.	38	
Pb	5.0	44.0	270	120
Bi	3.0	48.0	300	

\*May be due to residuals in mass spectrometer



The cupric fluoride analysis showed several impurities at levels greater than 100 ppm. Fe, Ni and Sn are present at very high levels; also excessive amounts of oxygen, chlorine, sulphur and carbon were found. Inasmuch as a promising purification method for the  $\text{CuF}_2$  does not exist, three alternatives present themselves: (1) use the present product  $\text{CuF}_2$  #2 as supplied, (2) test other commercially available products, and (3) synthesize anhydrous  $\text{CuF}_2$  at Rocketdyne. The last of these is being attempted.

#### Purity of Other Solutes and Water

Lithium bromide (LiBr #2; 99.99 percent, optical grade, Gallard-Schlesinger Chemical Manufacturing Corp.), dried at elevated temperature under vacuum, is being used. No extensive analysis of this chemical will be made because only its equivalent conductance at infinite dilution will be measured for the purpose of arriving at individual ion mobilities of other solutes; the same approach will also apply to tetrabutylammonium bromide (TBA·Br #1, polarographic grade, Columbia Organics) and to sodium tetraphenylboron ( $\text{Na} \cdot \text{TPhB}$  #1, reagent grade, Baker & Adamson).

Deionized distilled water with a typical conductivity of  $5 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  is being used. A further characterization is not justified as long as the water is added to the electrolytes only in small amounts, i.e., in amounts up to the 1000 ppm level.

#### Analysis of Solvents and Solutions by Vapor Phase Chromatography

A preliminary study was made to establish if the water content of a 1M  $\text{LiClO}_4/\text{PC}$  solution could be determined, using the procedure developed for determining water in pure propylene carbonate. Several aliquots of the



solution were injected into an Aerograph 660 gas chromatograph equipped with a 3 16-inch x 6-foot Porapak Q column, and the resulting peaks were compared to the peaks obtained with aliquots of the solvent used to prepare the solution. The size and shape of the water peaks found for the solution and the solvent were the same. Because the presence of lithium perchlorate does not distort the water peak, it would appear that evaporation of water from the surface of the salt is rapid at the injector temperature and that the method may be quantitative. The fact that the same amount of water was found in the solvent and solution seems to indicate that no water was retained by the lithium perchlorate. Further work must be done to demonstrate conclusively that the analysis of the solution for water is quantitative.

There was some concern about injecting an organic solvent containing perchlorate salts because of a possible oxidation of the solvent to carbon dioxide and water. However, the size of carbon dioxide peak was the same for the solvent and the solution.

The study of the determination of water in solutions was interrupted to analyze a new batch of dimethyl formamide. Prior to performing the analysis, the injection port and the 6-inch x 1 8-inch stainless-steel line that connects the column and the injector were rinsed with distilled water to remove any salt residue. The chromatograph was reassembled and allowed to equilibrate overnight. On the following day, the sample of dimethyl formamide was analyzed. The resulting water peak showed considerable tailing and the peak area increased with continued injections. Because this behavior is unlike any seen previously, it was assumed that the column had been contaminated by the previous experiments with the  $\text{LiClO}_4$  PC solution. Three possible explanations of the tailing are: (1) the lithium perchlorate salt could have completely dried during the overnight equilibration of the



instrument and the presence of the anhydrous salt may have caused the difficulties; (2) lithium perchlorate may have been reduced at 165 C by the hydrogen carrier gas and the resulting lithium chloride may have caused the difficulties; or (3) lithium perchlorate may have oxidized the Porapak Q packing material, giving the column a polar character. In any case, some lithium perchlorate must have been carried out of the injector and deposited on the column. The lithium perchlorate may have been swept out of the injection port as particulate matter or, more likely, the large sample may not have been completely evaporated in the injector and was pushed out of the injector and onto the column as a solution. In future experiments involving solutions, a second column will be placed between the injector and the Porapak Q column. This column will be packed with an inert material such as Teflon-6 or glass beads. The second column will be very short, and will be used to prevent any salt from reaching the Porapak Q column.

A new Porapak Q column was prepared which has the same dimensions and the same retention time for water as the old column (Ref. 3). The peak for water in dimethyl formamide has the same shape as the peak reported previously (Ref. 2). The new column has better characteristics than the old because it gives a better separation of acetonitrile and water. Also, a single peak was obtained for water in propylene carbonate under conditions where the older column had given two peaks (Ref. 1). It is hypothesized that the older column contained a material that catalyzed the hydrolysis of propylene carbonate.

The initial portion of a chromatogram of acetonitrile is shown in Fig. 1 (disturbances prior to the air peak are due to pressure surges caused by injecting a large sample). Due to the better separation of acetonitrile and water on the new column, the water peak returns to the baseline before

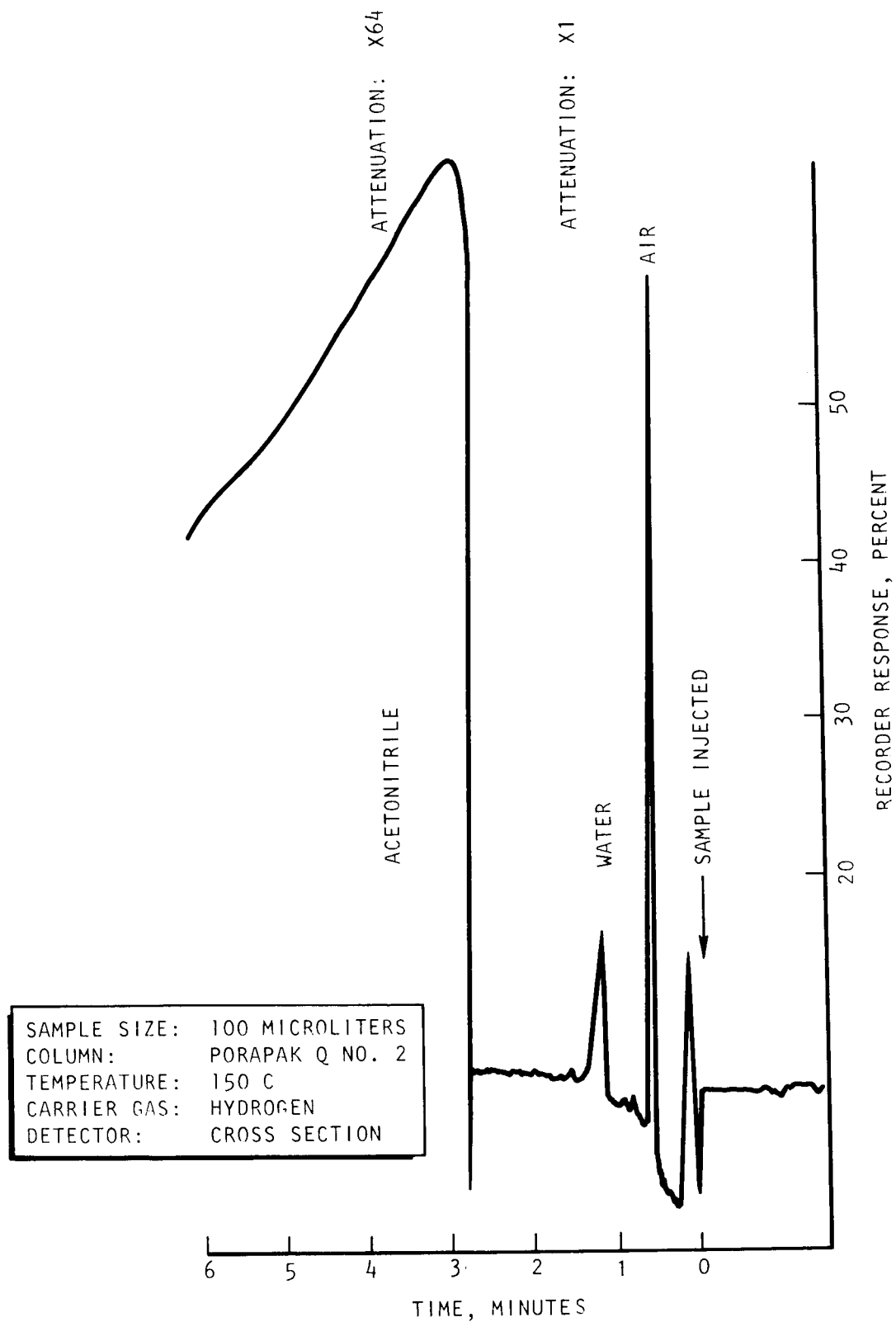


Figure 1. Initial Portion of Chromatogram of Acetonitrile on New Porapak Q Column





the initial portion of the acetonitrile peak; this was not the case on the older column. Previously, it was necessary to extrapolate the water peak under the acetonitrile peak to measure the area of the water peak. The response of the microcross-section detector to water in acetonitrile was determined by adding a measured volume of water to a weighed amount of acetonitrile. Using 100-microliter sample sizes, the response was found to be 92 ppm/cm<sup>2</sup> compared to the previous value of 112 ppm/cm<sup>2</sup> (Ref. 3). The response for water in propylene carbonate was found to be unchanged. The difference found in the case of acetonitrile is due to the better separation of water and acetonitrile on the new column.

#### NUCLEAR MAGNETIC RESONANCE STRUCTURAL STUDIES

##### Tetramethylammonium Hexafluorophosphate (TMA·PF<sub>6</sub>) In Dimethyl Formamide

The P-F splittings for PF<sub>3</sub>, PF<sub>5</sub>, PF<sub>6</sub><sup>-</sup>, and HPF<sub>6</sub> have been reported (Ref. 4) as 1441, 916, 710, and 710 Hz, respectively. Also, the P-F splitting for PF<sub>5</sub> complexed with amides has been reported as 740 Hz (Ref. 5). Because of the latter, the F<sup>19</sup> doublet found when TMA·PF<sub>6</sub> is dissolved in DMF (Ref. 3) was reinvestigated. The P-F splitting was measured and found to be 711 Hz, which agrees very well with that reported for PF<sub>6</sub><sup>-</sup>. No evidence of F-F splitting could be observed; the spectrum was a doublet only. Thus, the spectra could not be due to HPF<sub>6</sub>. This measurement corroborates and reinforces the previous report of the F<sup>19</sup> containing species as PF<sub>6</sub><sup>-</sup> (Ref. 3).



### LiClO<sub>4</sub> in Propylene Carbonate

Observation of the Cl<sup>35</sup> resonance of the ClO<sub>4</sub><sup>-</sup> ion has been reported (Ref. 7) in perchloric acid solutions containing a variety of ionic impurities. At low impurity concentrations the line width is relatively small, less than 0.5 gauss. Cl<sup>35</sup> has a spin 3/2, a quadrupole moment, and is not a particularly sensitive nucleus for NMR measurements. Therefore, the environment of the Cl<sup>35</sup> nucleus must be quite symmetrical if a resonance is found. In these solutions ClO<sub>4</sub><sup>-</sup> ion presents a tetrahedral symmetry at the Cl site, thus permitting the Cl<sup>35</sup> resonance to be observed and, because O<sup>16</sup> does not have a nuclear moment, the line is expected to be rather narrow as reported.

Preliminary observation of the Cl<sup>35</sup> resonance in ~1M LiClO<sub>4</sub> #2/PC #2-7 has been made, and the line is shown in Fig. 2. The line width is about 0.4 gauss. There may be some contribution to the line width due to modulation effects, and it is planned to investigate this during the next quarter.

In view of the reported work discussed above, it appears that dissolving LiClO<sub>4</sub> in PC produces ClO<sub>4</sub><sup>-</sup> ions, as is expected.

### CuCl<sub>2</sub> in Dimethyl Formamide and Propylene Carbonate

The high-resolution H<sup>1</sup> spectrum was investigated in the following specimens:

1. 1.00 M CuCl<sub>2</sub> #2/DMF #3-3
2. 0.005 M (saturated at 25 C) CuCl<sub>2</sub> #2/PC #2-6



Figure 3 shows the  $H^1$  spectrum for 1.00 M  $CuCl_2/DMF$ . The field scanned in obtaining this spectrum corresponds to several times the scan required to produce the entire  $H^1$  spectrum in pure DMF (Ref. 3). The  $H^1$  spectrum in DMF has been greatly broadened, which is characteristic of the introduction of paramagnetic impurities. Thus,  $CuCl_2$  dissolved in DMF produces a paramagnetic species, probably  $Cu^{++}$ . In addition to the very large line broadening, the addition of  $CuCl_2$  produces a down field shifted peak showing that a coordinating species is produced. The down field shift is very large, 840 Hz, which is characteristic of isotropic hyperfine contact interactions with paramagnetic species, showing that the DMF is coordinated with the paramagnetic species.

The NMR for paramagnetic species is shifted by very large amounts so that the resonance does not occur at the frequency, for a given external magnetic field, corresponding to its nuclear magnetic moment. A scan was made for the  $Cu^{63}$  resonance in specimen 1 at the magnetic field and frequency corresponding to the  $Cu^{63}$  magnetic moment. A weak, broad line was found, thus showing that there are two copper-containing species formed when  $CuCl_2$  is dissolved in DMF. One is paramagnetic, the one coordinating DMF molecules, and the other is a nonparamagnetic species. Whether the nonparamagnetic species coordinates DMF cannot be determined because of the large effects of the paramagnetic species.

The low solubility of  $CuCl_2$  in PC resulted in no change in the  $H^1$  spectrum of specimen 2 so that it was found identical to that in pure PC (Fig. 7).

#### $LiCl + AlCl_3$ in Propylene Carbonate and Acetonitrile

Both high-resolution  $H^1$  and wideline  $Al^{27}$  resonances were investigated in these systems.

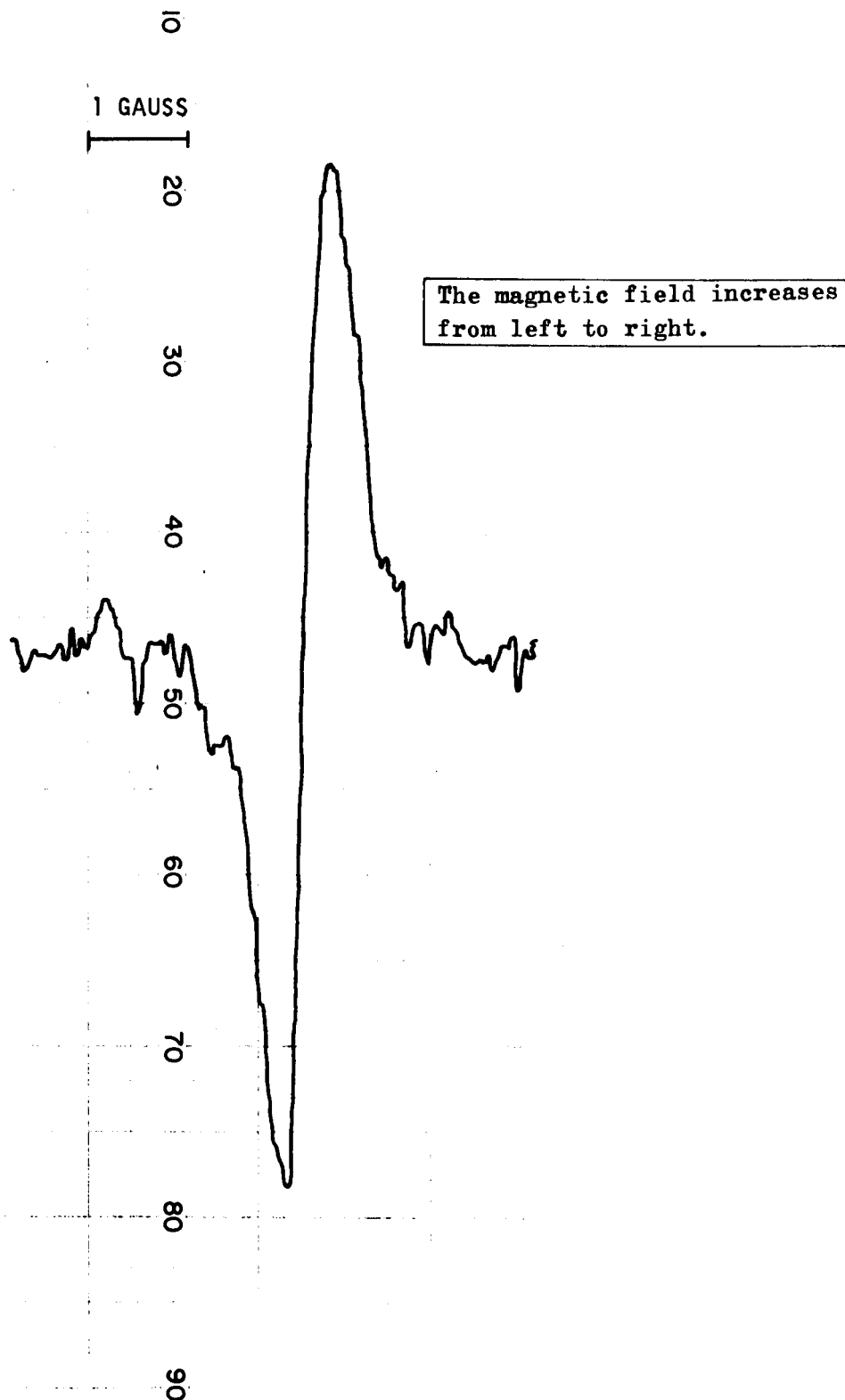


Figure 2.  $\text{Cl}^{35}$  Resonance in 1 M  $\text{LiClO}_4/\text{PC}$

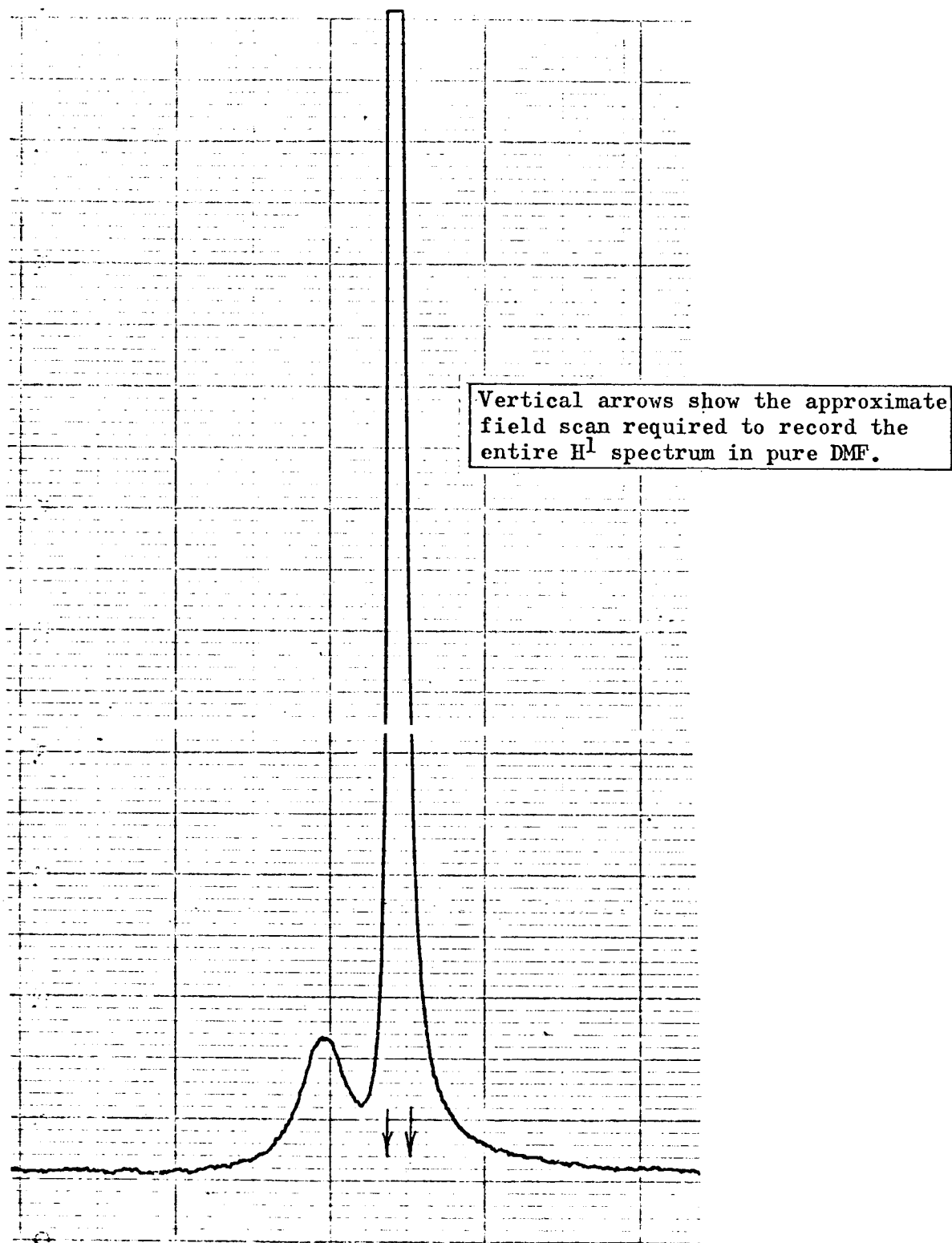


Figure 3.  $H^1$  Spectrum in 1.00 M  $CuCl_2/DMF$



The high-resolution  $H^1$  resonance spectrum was investigated in the following specimens:

1. Pure AN #3-1
2. 0.983 M  $AlCl_3$  #3/AN #3-1
3. 0.9 M (saturated at 25 C) LiCl #2 in 0.983 M  $AlCl_3$  #3/AN #3-1
4. Pure PC #2-6
5. 1.00 M  $AlCl_3$  #3/PC #2-6
6. 0.7 M (saturated at 25 C) LiCl #2 in 1.00 M  $AlCl_3$  #3/PC #2-6

As can be seen in Fig. 4, 5, 7, 8, and 9, down field shifted peaks due to coordinated solvent molecules are observed in both PC and AN. Thus,  $AlCl_3$  dissolved in either AN or PC produces a species which coordinates the solvent molecules; the same behavior had been shown previously to occur with  $AlCl_3$  dissolved in DMF (Ref. 3). When sufficient LiCl to form a saturated solution is added to these solutions, the  $H^1$  spectrum for either PC or AN returns to the spectrum obtained for the pure solvents (Fig. 6 for AN; spectrum for specimen 6 not shown but identical to Fig. 7). The addition of LiCl to the solution results in the disappearance of the coordinating species. This did not occur in DMF (Ref. 3).

The  $Al^{27}$  resonance was investigated at a magnetic field of 7120 gauss, using a broadline spectrometer, in specimens 2, 3, 5, and 6. Recorded spectra (derivatives of the absorption lines) for specimens 5 and 6 are shown in Figs. 10 and 11, respectively. As displayed in Fig. 10, two  $Al^{27}$  lines are obtained from the 1.00 M  $AlCl_3$ /PC solution, showing that there are two inequivalent aluminum atom environments present. If there is one aluminum atom per ionic (or neutral) species, this means that

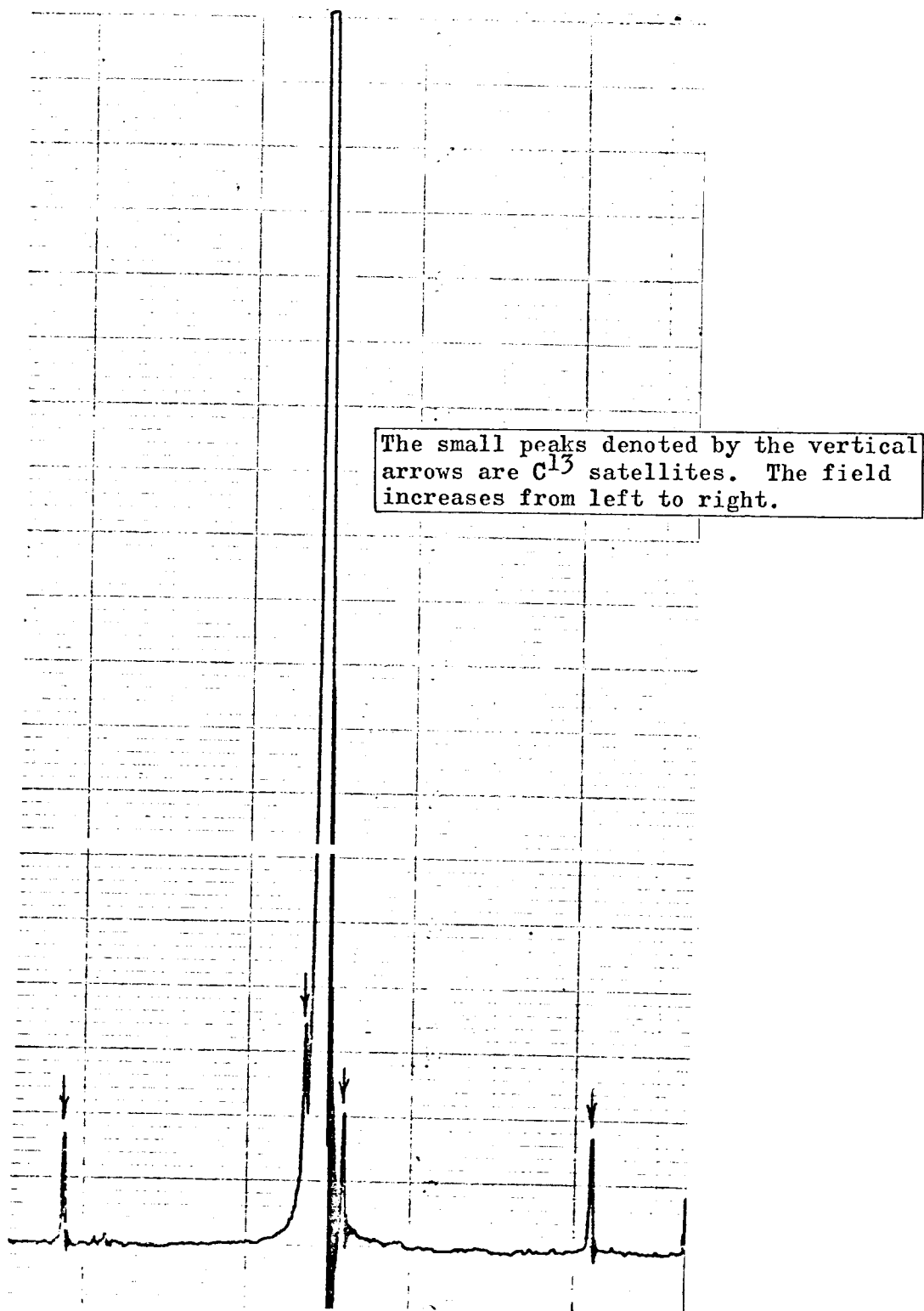


Figure 4. High-Resolution  $H^1$  Spectrum in Pure AN

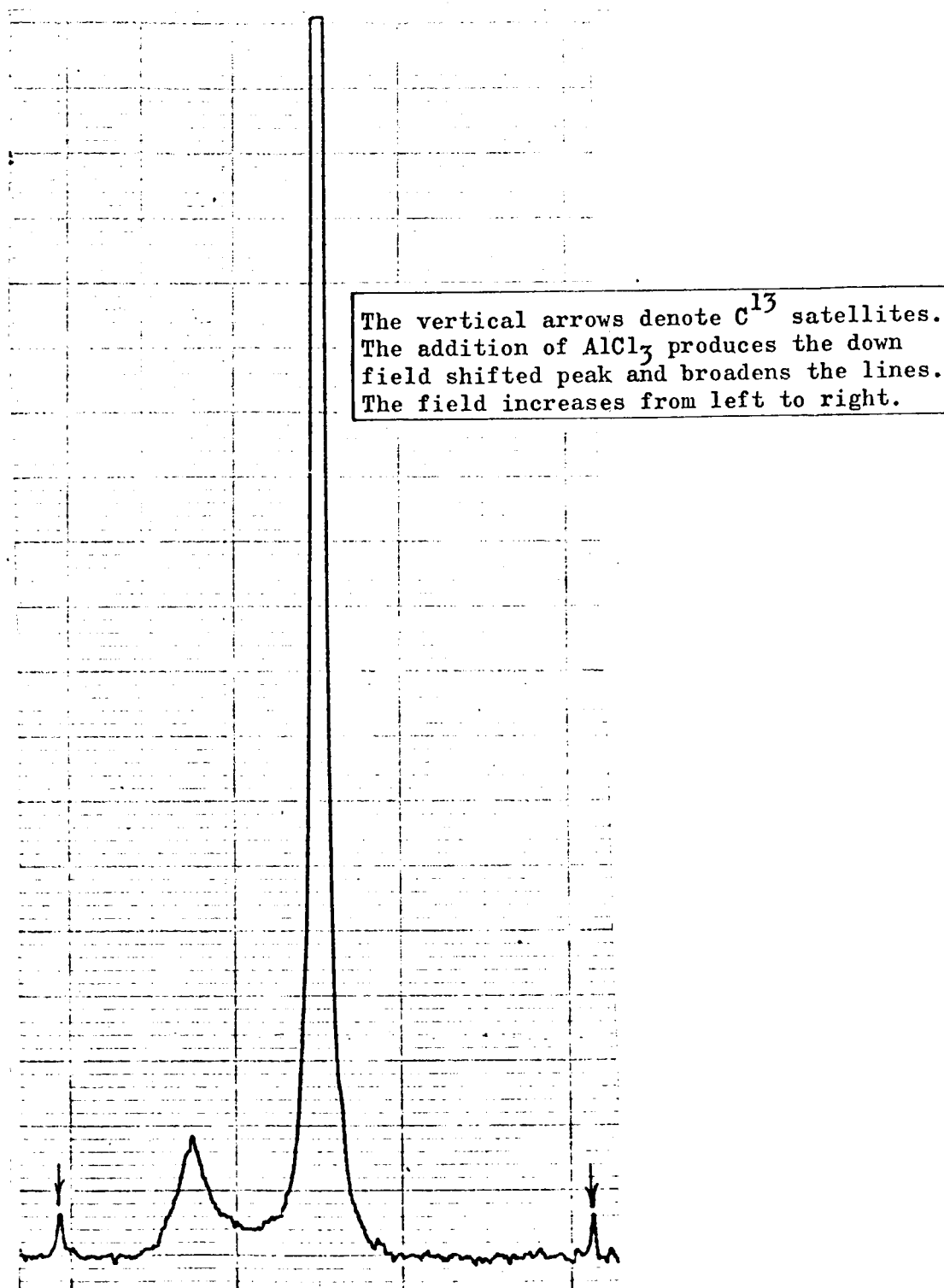


Figure 5. High-Resolution  $H^1$  Spectrum in 0.983 M  $AlCl_3/AN$



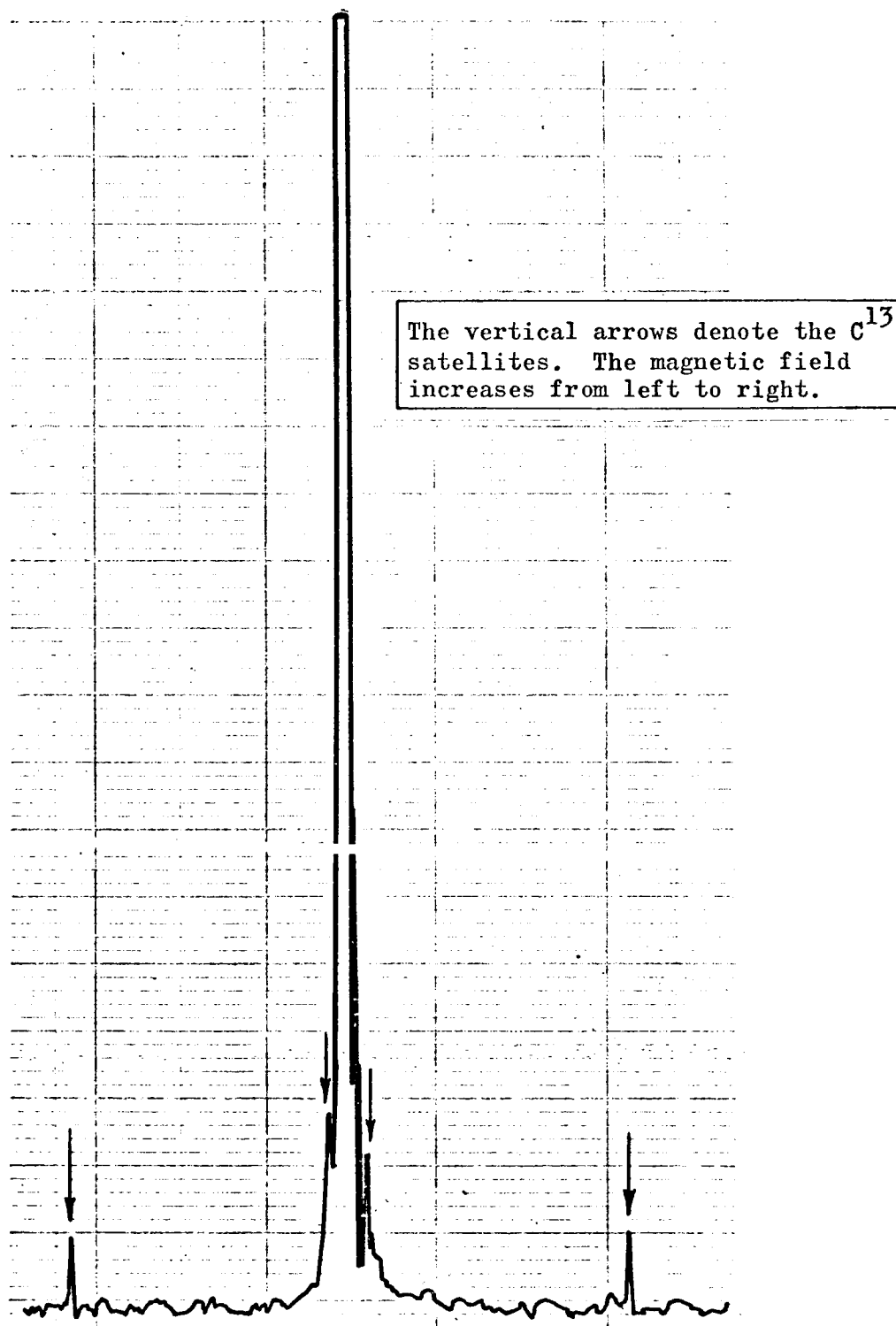


Figure 6. High-Resolution  $H^1$  Spectrum in 0.983 M  $AlCl_3/AN$  Saturated With  $LiCl$

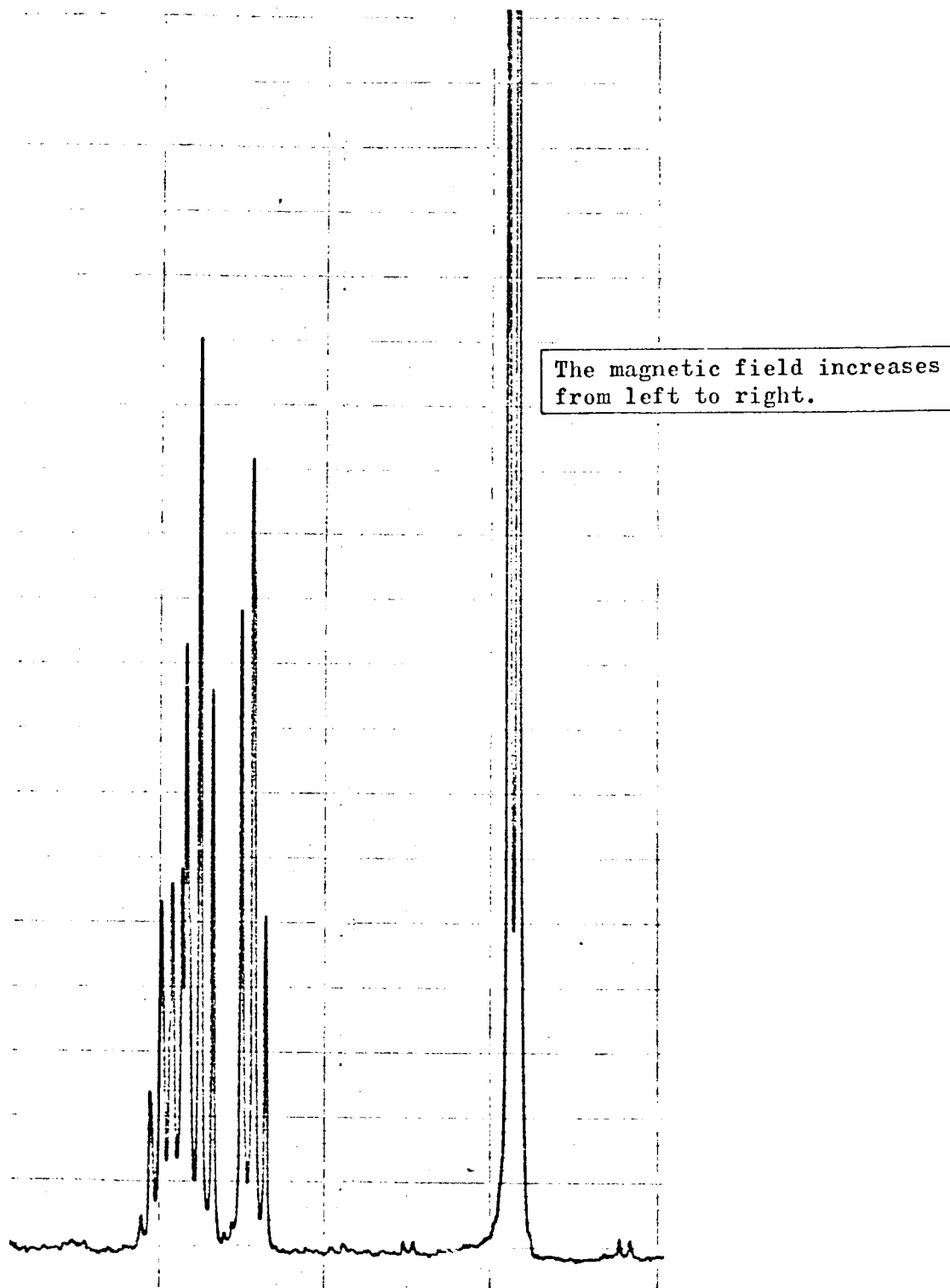


Figure 7. High-Resolution  $^1\text{H}$  Spectrum in Pure PC

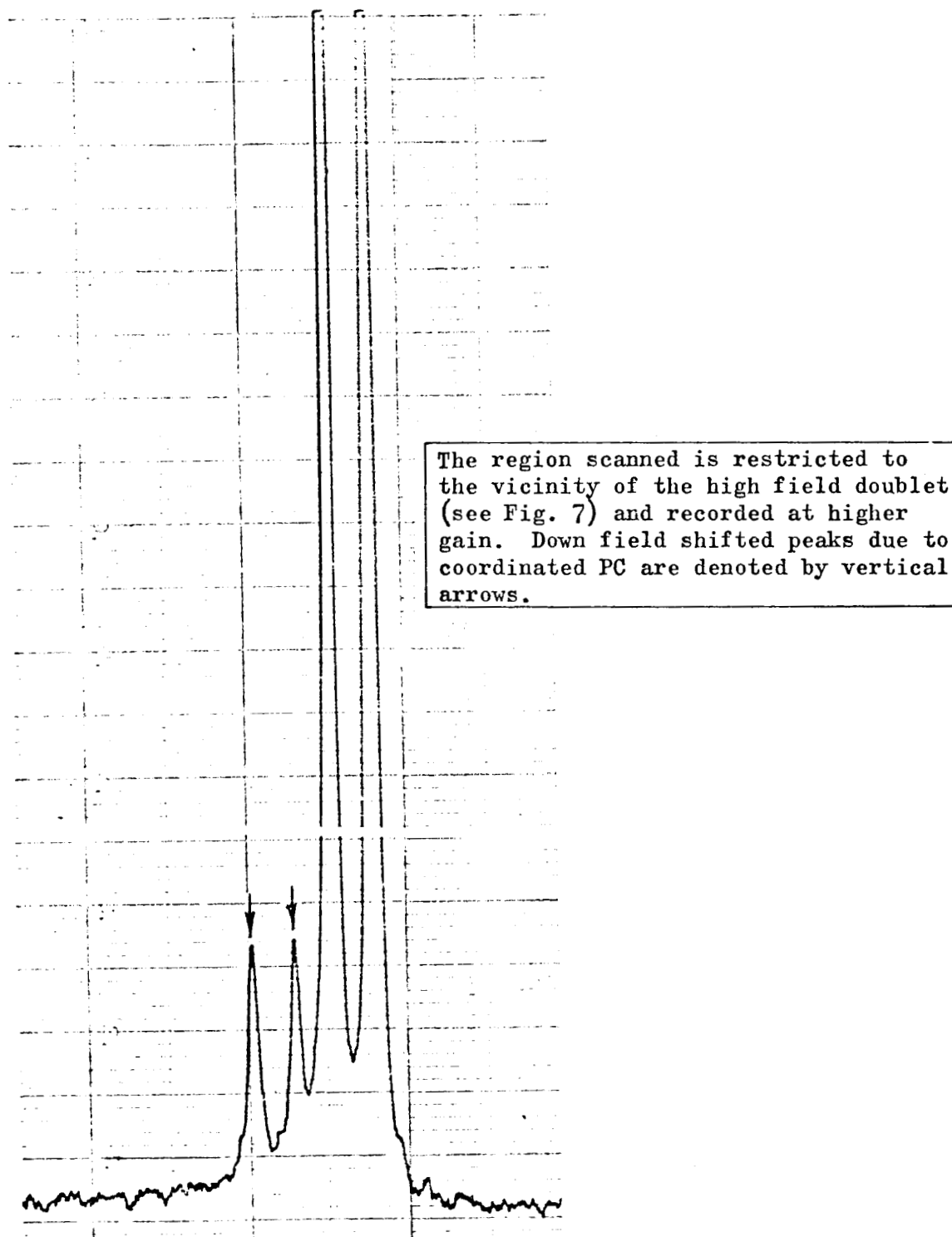


Figure 8. High-Resolution  $H^1$  Spectrum in 1.00 M  $AlCl_3/PC$

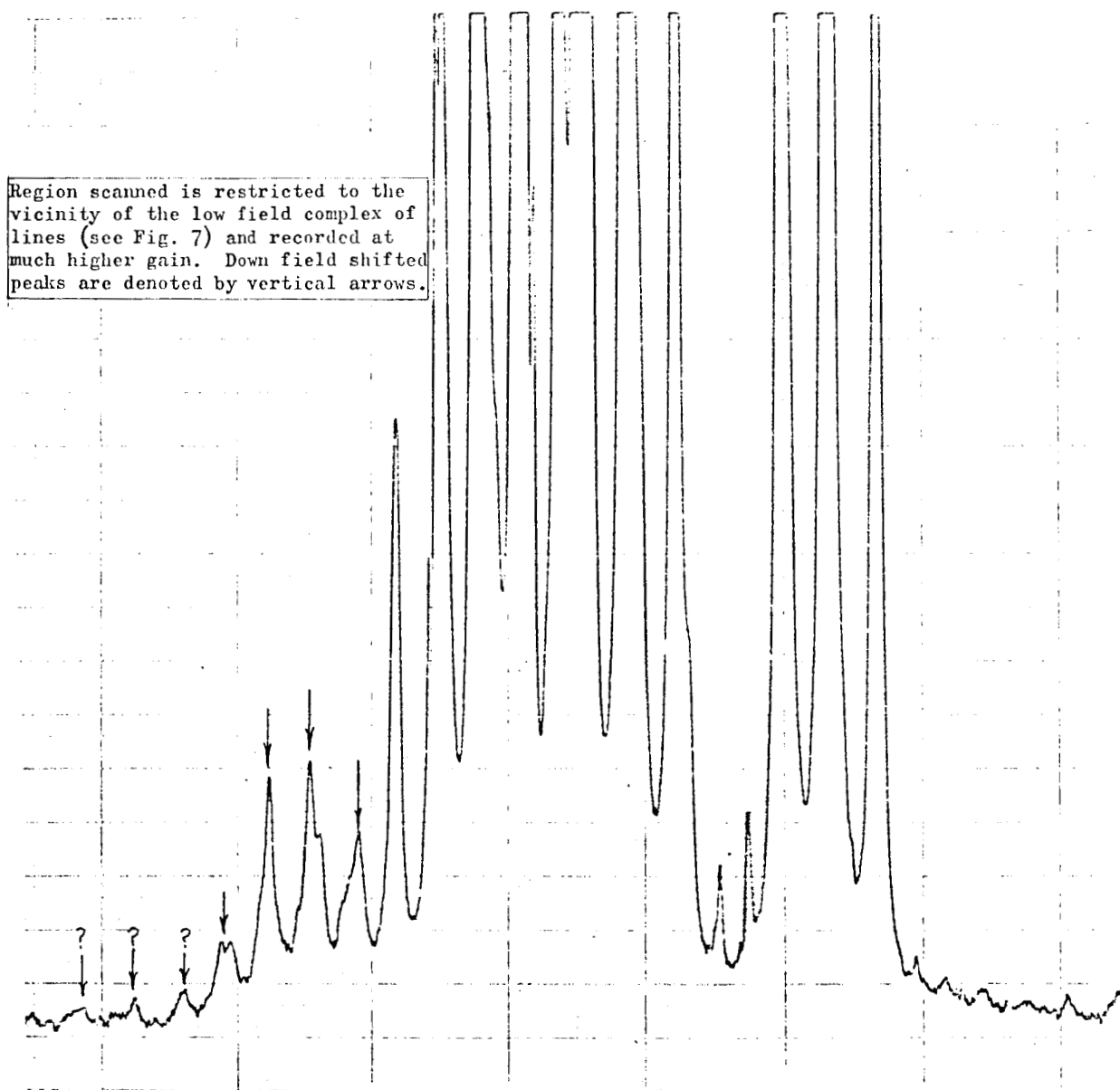


Figure 9. High-Resolution  $H^1$  Spectrum in 1.00 M  $AlCl_3/PC$



there are two species present. The line width of both of these lines is quite small, but accurate measurements have not been made as yet. Since the  $\text{Al}^{27}$  nucleus has a quadrupole moment of moderate magnitude, the observation of narrow lines indicates that the  $\text{Al}^{27}$  nuclei are located at sites having tetrahedral or octahedral symmetry. The lines are not equally intense, showing that one species is more prevalent than the other. Figure 11 shows that the addition of  $\text{LiCl}$  causes one of the species to disappear because only one of the lines is observed.

Two specimens, 5 and 6, were prepared with external references for chemical shift measurements. The external reference was an acidic aqueous solution of  $\text{AlCl}_3$  which yields  $\text{Al}(\text{H}_2\text{O})_6^{+++}$  (Ref. 7). The less intense peak found in specimen 1 was just barely shifted from the reference signal; the more intense line was shifted about 95 ppm down field. In specimen 2, the remaining peak was about 95 ppm down field from the reference signal and more intense; thus, it appears that the addition of  $\text{LiCl}$  to  $\text{AlCl}_3/\text{PC}$  causes the less prevalent species to be converted to the more prevalent species.

Similar results were found in the AN solutions; i.e., two lines in specimen 2 and one line in specimen 3. However, a white precipitate formed in specimen 3, casting some doubt on the usefulness of the spectra obtained from this specimen.

It is still premature to make species assignments in these specimens. However, the results are not in complete agreement with species suggested in Ref. 8.  $\text{AlCl}_4^-$  presumably has tetrahedral symmetry and would therefore give rise to a narrow  $\text{Al}^{27}$  resonance line. Thus, this species may be one of the observed species; however, the complex species containing  $\text{AlCl}_2 \cdot (\text{AlCl}_3)_n^+$  suggested in Ref. 8 would give rise to broad  $\text{Al}^{27}$  lines which were not observed. Thus, this type of species is not present.

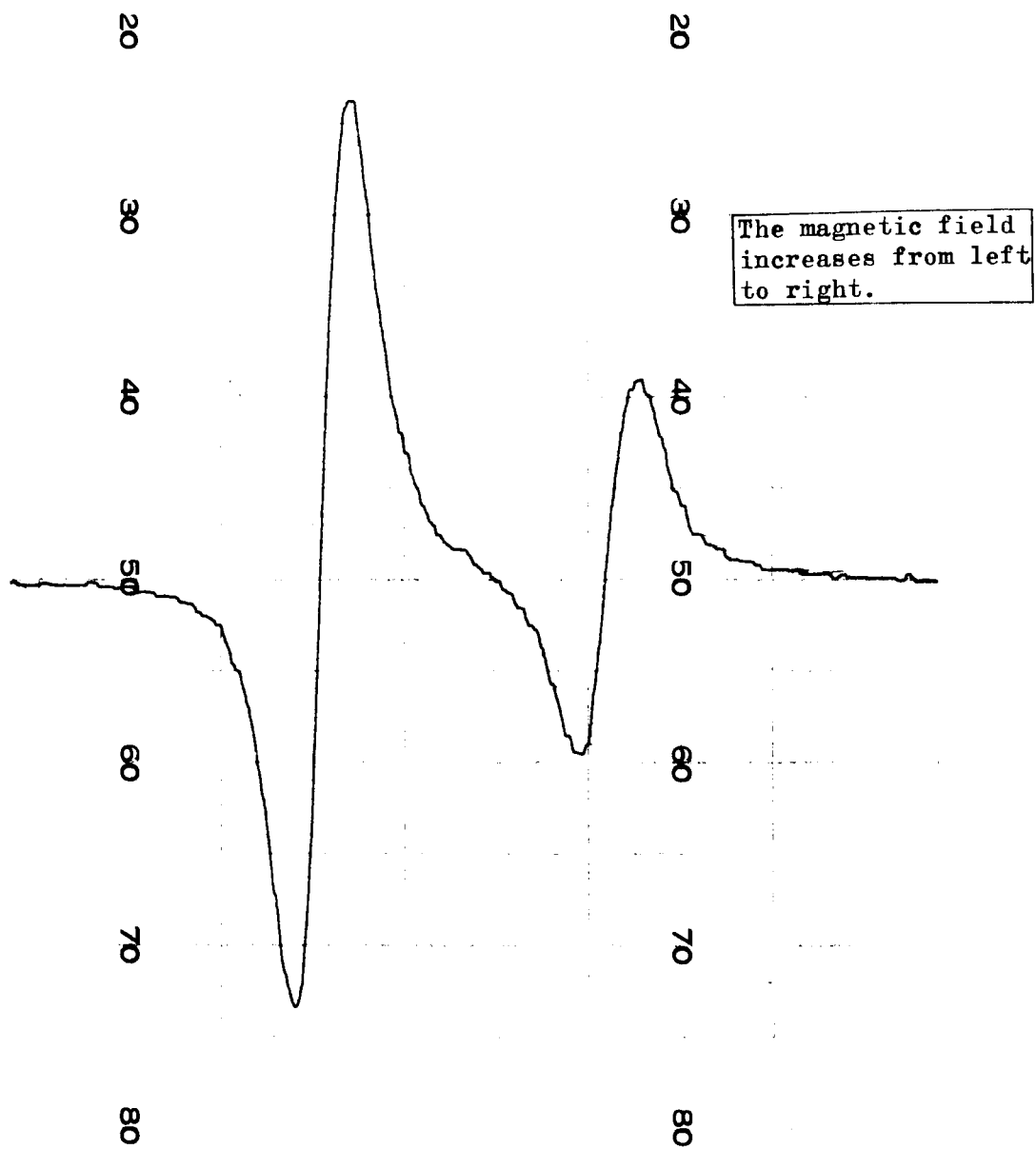


Figure 10.  $\text{Al}^{27}$  Resonance in 1.00 M  $\text{AlCl}_3/\text{PC}$

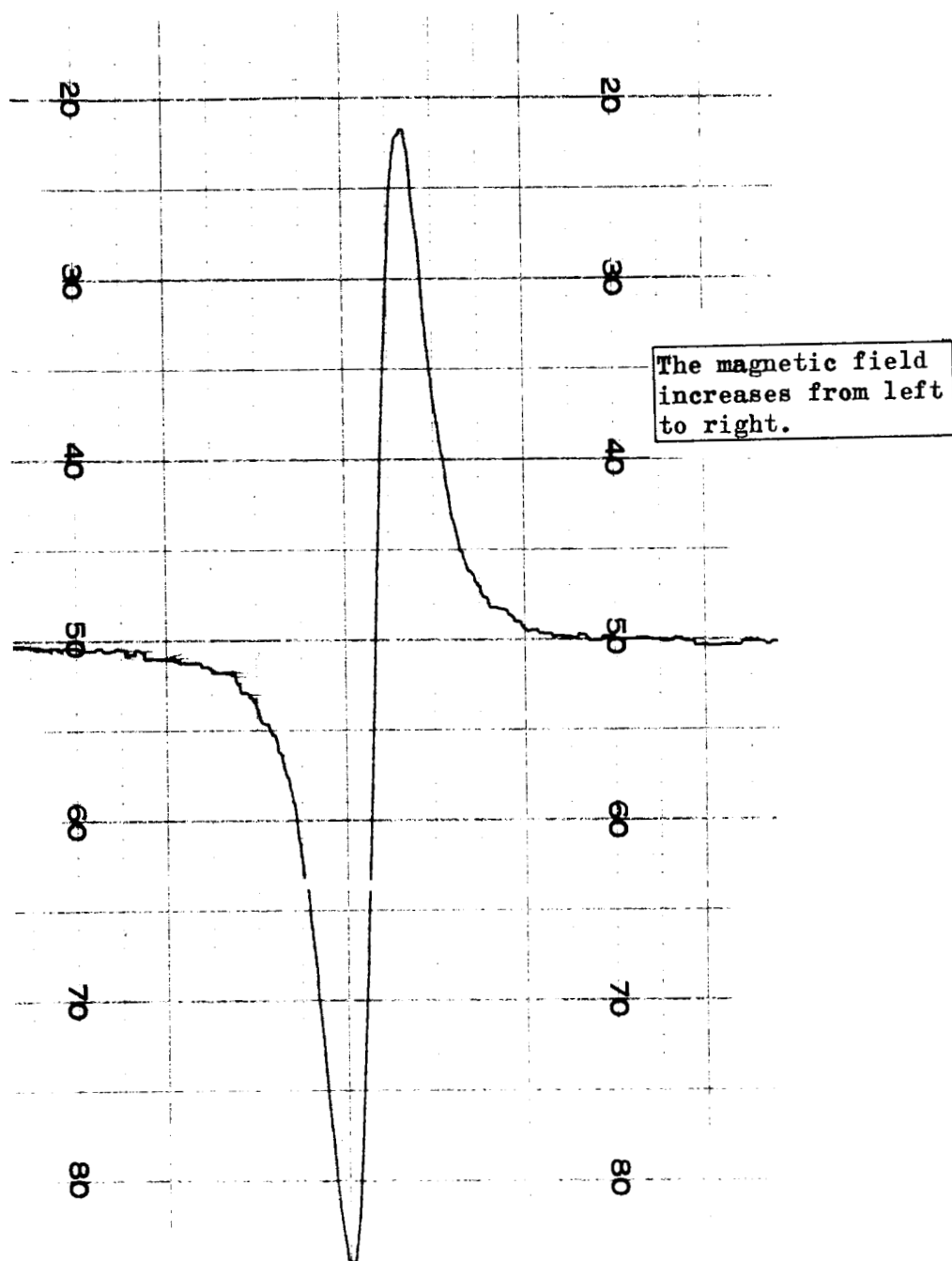


Figure 11.  $\text{Al}^{27}$  Resonance in 0.7M (Saturated at 25 C) LiCl in  
1.00M  $\text{AlCl}_3/\text{PC}$



The broadening displayed in the spectrum in Fig. 5 ( $\text{AlCl}_3/\text{AN}$ ) is probably a result of exchange between coordinated and bulk AN molecules. When there are two chemically unequivalent chemical sites for the resonating nucleus, in this case  $\text{H}^1$ , the spectrum can be very sensitive to the exchange rates between the two sites. The analysis of the situation is described in Ref. 9 under conditions of very slow, very fast, and intermediate rates of exchange. In the case of slow exchange, separate resonances are observed, which is the case in this spectrum. Under these circumstances the transverse relaxation time,  $\tau_2$ , of one of the lines (designated by A) is given by

$$\tau_{2A}^{-1} = T_{2A}^{-1} + \tau_A^{-1}$$

where

$T_{2A}$  = relaxation time in site A without exchange

$\tau_A$  = first-order lifetime in site A

A similar expression holds for the second site, B:

$$\tau_{2B}^{-1} = T_{2B}^{-1} + \tau_B^{-1}$$

From the recorded spectra the resonant frequency shift between the two sites,  $\omega_A - \omega_B$ , is 30.0 Hz,  $\tau_{2B}^{-1}$  is 31.4  $\text{sec}^{-1}$ , and  $\tau_{2A}^{-1}$  is approximately 3.8  $\text{sec}^{-1}$ .  $\tau_{2B}^{-1}$  is taken from the line width at half maximum.  $\tau_{2A}^{-1}$  is estimated from the broadening of the line such that the  $\text{C}^{13}$  satellites, clearly shown in the spectrum of neat AN (Fig. 3), are just smeared out as displayed in the spectrum of Fig. 4. From the neat AN spectrum,





$T_2^{-1} = 1.8 \text{ sec}^{-1}$ . Only approximate values are used here for qualitative discussion. The assignments A and B correspond to the bulk and the coordinated AN molecules, respectively. From these data,  $\tau_A \doteq 0.54$  second. To obtain  $\tau_B^{-1}$ ,  $T_{2B}$  for this site is required, but it can only be obtained when no exchange is present.\* It seems reasonable to assume that it is not too different from  $T_{2A}^{-1}$ . Under this assumption,  $\tau_B \doteq 0.05$  second. This long lifetime corresponds to a very slow exchange rate of coordinated AN molecules with bulk AN molecules.

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\* $T_{2B}$  can be obtained, in principle, by making measurements at low temperatures to further slow down exchange rates. Such measurements are planned.



## PHYSICAL PROPERTY DETERMINATIONS

Viscosity Measurements

Viscosities were determined by the method described in the previous quarterly report (Ref. 5). The results are presented in Table 4.

TABLE 4

## VISCOSITY DETERMINATIONS AT 25 C

Solute	Concentration	Solvent	Density, gm/cc	Viscosity, millipoise
LiCl #2 +AlCl <sub>3</sub> #5	Saturated (0.92 M) 1.00 M	AN #5-1	0.879	6.69
LiClO <sub>4</sub>	1.00 M	PC #2-6	1.254	70.8
LiClO <sub>4</sub>	1.00 M	DMF #3-5	1.019	18.9
LiClO <sub>4</sub>	1.00 M	AN #3-2	0.863	6.60

Solubility Measurements

The analytical procedures used to measure the solubilities of the various solutes were described previously (Ref. 5). The solubility data collected during this report period are presented in Table 5.

The value of 0.92 M for the solubility of LiCl in 1 M AlCl<sub>3</sub>/AN may be compared to the value of 0.025 M found for LiCl in AN alone (Ref. 5). These results suggest a strong interaction between LiCl and AlCl<sub>3</sub> in the acetonitrile system. The same situation had been observed in propylene carbonate (Ref. 5), and an interaction is indeed also evident from NMR measurements



TABLE 5

## SOLUBILITY DETERMINATIONS

Solute	Solvent	Temperature, C	Procedure	Solubility, molar
LiCl #2	1 M AlCl <sub>3</sub> #3/AN #3-1	25	Chloride Titration	0.92
LiClO <sub>4</sub> #2	PC #2-7	25 60	Atomic Absorption	2.1 3.1
LiClO <sub>4</sub> #2	PC #2-7, 1000 ppm H <sub>2</sub> O	25 60	Atomic Absorption	3.1 3.1
LiClO <sub>4</sub> #2	DMF #3-3	25 60	Atomic Absorption	4.4 4.8
LiClO <sub>4</sub> #2	DMF #3-3, 1000 ppm H <sub>2</sub> O	25 60	Atomic Absorption	3.5 4.9
CuCl <sub>2</sub> #2	1 M LiClO <sub>4</sub> #2/PC #2-7	25 60	Atomic Absorption	1.89 x 10 <sup>-3</sup> 4.18 x 10 <sup>-3</sup>
CuCl <sub>2</sub> #2	1 M LiClO <sub>4</sub> #2/PC #2-8, 1000 ppm H <sub>2</sub> O	25 60	Atomic Absorption	1.07 x 10 <sup>-2</sup> 1.92 x 10 <sup>-2</sup>
CuCl <sub>2</sub> #2	1 M AlCl <sub>3</sub> #3+Saturated LiCl #2/PC #2-8	25 60	Atomic Absorption	0.37 0.57
CuCl <sub>2</sub> #2	1 M LiClO <sub>4</sub> #2/DMF #3-3	25 60	Atomic Absorption	0.82 1.57
CuCl <sub>2</sub> #2	1 M LiClO <sub>4</sub> #2/DMF #3-5, 1000 ppm H <sub>2</sub> O	25 60	Atomic Absorption	0.87 2.2
TMAF <sub>6</sub> #1	PC #2-6, 1000 ppm H <sub>2</sub> O	25 60	Nuclear Magnetic Resonance	0.15 0.23
TMAF <sub>6</sub> #1	DMF #3-3, 1000 ppm H <sub>2</sub> O	25 60	Nuclear Magnetic Resonance	0.21 0.32



in these two solvents. A similar phenomenon of increased solubility for  $\text{CuCl}_2$  occurred in 1 M  $\text{AlCl}_3$  + saturated  $\text{LiCl}/\text{PC}$ .

The addition of 1000 ppm water did not appear to affect the solubilities in an entirely predictable manner. In the case of the slightly soluble  $\text{CuCl}_2$  in 1 M  $\text{LiClO}_4/\text{PC}$ , an increase in solubility by a factor of 5 was obtained upon addition of 1000 ppm water, whereas the solubility of  $\text{TMA}\cdot\text{PF}_6$  in PC was unaffected, and the solubility value of  $\text{TMA}\cdot\text{PF}_6$  in DMF was decreased slightly (compare to values given in Ref. 3). In the case of solutes of high solubility, no significant effects were observed.

#### Conductance Measurements

The conductance measurements made during this report period are presented in Tables 6 through 10 and in Fig. 12 through 18.

The equivalent (molar) conductance values at infinite dilution,  $\Lambda_0$ , for  $\text{LiClO}_4/\text{PC}$  ( $25.6 \text{ ohm}^{-1} \text{ equ}^{-1} \text{ cm}^2$  at 25 C and 43.1 at 60 C) are close to the ones obtained for  $\text{LiCl}/\text{PC}$  (26.2 and 44.9, respectively; Ref. 3). A value of  $26.39 \text{ ohm}^{-1} \text{ equ}^{-1} \text{ cm}^2$  is given by Boden (Ref. 10) for  $\text{LiClO}_4/\text{PC}$  at 25 C.

The  $\Lambda_0$  values for  $\text{LiClO}_4/\text{AN}$  were  $172 \text{ ohm}^{-1} \text{ equ}^{-1} \text{ cm}^2$  at 25 C and 220 at 60 C. The differences between the corresponding  $\Lambda_0$  values in the two solvents can be explained readily by considering the differences of the solvent viscosities. The same holds for the results obtained with  $\text{LiBr}$  in propylene carbonate and dimethyl formamide.

The equivalent (molar) conductance at infinite dilution for a solution containing  $\text{AlCl}_3$  and  $\text{LiCl}$  in AN was  $148 \text{ ohm}^{-1} \text{ equ}^{-1} \text{ cm}^2$  at 25 C and 188 at 60 C. These figures are indicative of a predominantly 1-1 electrolyte; the species present probably are  $\text{Li}^+$  and  $\text{AlCl}_4^-$ .



TABLE 6

SPECIFIC CONDUCTANCE ( $\lambda$ ) AND EQUIVALENT CONDUCTANCE ( $\Lambda$ )  
OF  $\text{LiClO}_4$  #2/PC #2-6 AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$ , $1/2$ molar	$\lambda$ (25 C), $\text{ohm}^{-1} \text{cm}^{-1}$	$\Lambda^*$ (25 C), $\text{ohm}^{-1} \text{equ}^{-1} \text{cm}^2$	$\lambda$ (60 C), $\text{ohm}^{-1} \text{cm}^{-1}$	$\Lambda^*$ (60 C), $\text{ohm}^{-1} \text{equ}^{-1} \text{cm}^2$
0.09996	0.9999	$5.363 \times 10^{-3}$	5.64	$1.055 \times 10^{-2}$	10.55
0.009996	0.3161	$1.697 \times 10^{-3}$	16.98	$2.872 \times 10^{-3}$	28.73
0.0009996	0.09999	$2.178 \times 10^{-4}$	21.78	$3.686 \times 10^{-4}$	36.85
0.004998	0.07067	$1.123 \times 10^{-4}$	22.45	$1.903 \times 10^{-4}$	38.04
0.002499	0.04999	$5.796 \times 10^{-5}$	23.15	$9.825 \times 10^{-5}$	39.22
0.001250	0.03535	$2.974 \times 10^{-5}$	23.70	$5.058 \times 10^{-5}$	40.27
0.0006250	0.02500	$1.522 \times 10^{-5}$	24.16	$2.587 \times 10^{-5}$	41.01
0.0003125	0.01768	$7.842 \times 10^{-6}$	24.70	$1.326 \times 10^{-5}$	41.66
0.0001562	0.01250	$3.924 \times 10^{-6}$	24.33	$6.705 \times 10^{-6}$	41.41
0		$1.241 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 25.6$	$2.359 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 43.1$

$\Lambda^*$  Equivalent conductance, corrected for conductance of pure solvent



TABLE 7

SPECIFIC CONDUCTANCE ( $\lambda$ ) AND EQUIVALENT CONDUCTANCE ( $\Lambda$ )  
OF  $\text{LiClO}_4$  #2/AN #3-2 AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$ , molar <sup>1/2</sup>	$\lambda$ (25 C), ohm <sup>-1</sup> cm <sup>-1</sup>	$\Lambda^*$ (25 C), ohm <sup>-1</sup> equ cm <sup>2</sup>	$\lambda$ (60 C), ohm <sup>-1</sup> cm <sup>-1</sup>	$\Lambda^*$ (60 C), ohm <sup>-1</sup> equ cm <sup>2</sup>
1.0014	1.0000	$3.177 \times 10^{-2}$	31.7	$5.909 \times 10^{-2}$	39.0
0.2003	0.4471	$1.479 \times 10^{-2}$	73.8	$1.767 \times 10^{-2}$	88.2
0.04006	0.2001	$4.429 \times 10^{-3}$	110.5	$5.411 \times 10^{-3}$	135.0
0.008012	0.08952	$1.110 \times 10^{-3}$	138.4	$1.393 \times 10^{-3}$	173.7
0.004006	0.06329	$5.919 \times 10^{-4}$	147.6	$7.478 \times 10^{-4}$	186.5
0.002003	0.04473	$3.110 \times 10^{-4}$	154.9	$3.940 \times 10^{-4}$	196.3
0.001001	0.03161	$1.607 \times 10^{-4}$	159.8	$2.046 \times 10^{-4}$	203.6
0.0005008	0.02238	$8.248 \times 10^{-5}$	163.4	$1.052 \times 10^{-4}$	208.5
0.0002504	0.01582	$4.217 \times 10^{-5}$	165.8	$5.389 \times 10^{-5}$	212.0
0.0001252	0.01119	$2.136 \times 10^{-5}$	165.4	$2.727 \times 10^{-5}$	211.3
0		$6.539 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 172$	$8.092 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 220$

$\Lambda^*$ Equivalent conductance, corrected for conductance of pure solvent



TABLE 8

SPECIFIC CONDUCTANCE ( $\lambda$ ) AND EQUIVALENT CONDUCTANCE ( $\Lambda$ )  
OF LiBr #2/PC AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$ , molar <sup>1/2</sup>	$\lambda$ (25 C), $\frac{\text{ohm}^{-1}}{\text{cm}}$	$\Lambda^*$ (25 C), $\frac{\text{ohm}^{-1}}{\text{equivalent cm}^2}$	$\lambda$ (60 C), $\frac{\text{ohm}^{-1}}{\text{cm}}$	$\Lambda^*$ (60 C), $\frac{\text{ohm}^{-1}}{\text{equivalent cm}^2}$
99.8 x 10 <sup>-4</sup> *	9.99 x 10 <sup>-2</sup>	2.166 x 10 <sup>-4</sup>	21.5	5.640 x 10 <sup>-4</sup>	36.2
49.9 x 10 <sup>-4</sup> *	7.06 x 10 <sup>-2</sup>	1.163 x 10 <sup>-4</sup>	23.0	1.969 x 10 <sup>-4</sup>	58.9
26.8 x 10 <sup>-4</sup> **	5.18 x 10 <sup>-2</sup>	6.371 x 10 <sup>-5</sup>	23.6	1.091 x 10 <sup>-4</sup>	40.3
24.9 x 10 <sup>-4</sup> *	4.99 x 10 <sup>-2</sup>	6.129 x 10 <sup>-5</sup>	23.9	1.041 x 10 <sup>-4</sup>	40.5
13.4 x 10 <sup>-4</sup> **	3.66 x 10 <sup>-2</sup>	3.322 x 10 <sup>-5</sup>	24.5	5.689 x 10 <sup>-5</sup>	42.0
12.5 x 10 <sup>-4</sup> *	3.53 x 10 <sup>-2</sup>	3.227 x 10 <sup>-5</sup>	24.5	5.511 x 10 <sup>-5</sup>	41.8
6.70 x 10 <sup>-4</sup> **	2.59 x 10 <sup>-2</sup>	1.716 x 10 <sup>-5</sup>	25.2	2.931 x 10 <sup>-5</sup>	42.9
6.24 x 10 <sup>-4</sup> *	2.50 x 10 <sup>-2</sup>	1.722 x 10 <sup>-5</sup>	24.8	2.931 x 10 <sup>-5</sup>	42.2
3.35 x 10 <sup>-4</sup> **	1.83 x 10 <sup>-2</sup>	8.873 x 10 <sup>-6</sup>	25.6	1.509 x 10 <sup>-5</sup>	43.4
3.08 x 10 <sup>-4</sup> *	1.76 x 10 <sup>-2</sup>	9.616 x 10 <sup>-6</sup>	25.5	1.633 x 10 <sup>-5</sup>	43.4
1.68 x 10 <sup>-4</sup> **	1.30 x 10 <sup>-2</sup>	4.621 x 10 <sup>-6</sup>	25.7	7.886 x 10 <sup>-6</sup>	43.6
1.54 x 10 <sup>-4</sup> *	1.231 x 10 <sup>-2</sup>	5.632 x 10 <sup>-6</sup>	25.2	9.489 x 10 <sup>-6</sup>	42.4
0*		1.754 x 10 <sup>-6</sup>		2.952 x 10 <sup>-6</sup>	
0**		3.019 x 10 <sup>-7</sup>	Extrapolated: $\Lambda_0 = 26.2$	5.596 x 10 <sup>-7</sup>	Extrapolated: $\Lambda_0 = 44.8$

\*PC #2-8

\*\*PC #2-7

 $\Lambda^*$ Equivalent conductance, corrected for conductance of pure solvent



TABLE 9

SPECIFIC CONDUCTANCE ( $\lambda$ ) AND EQUIVALENT CONDUCTANCE ( $\Lambda$ )  
OF LiBr #2/DMF #3-4 AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$ , molar <sup>1/2</sup>	$\lambda$ (25 C), ohm <sup>-1</sup> cm <sup>-1</sup>	$\Lambda^*$ (25 C), ohm <sup>-1</sup> equ <sup>-1</sup> cm <sup>2</sup>	$\lambda$ (60 C), ohm <sup>-1</sup> cm <sup>-1</sup>	$\Lambda^*$ (60 C), ohm <sup>-1</sup> equ <sup>-1</sup> cm <sup>2</sup>
$79.76 \times 10^{-4}$	$8.93 \times 10^{-2}$	$5.194 \times 10^{-4}$	65.1	$7.213 \times 10^{-4}$	90.4
$39.88 \times 10^{-4}$	$6.32 \times 10^{-2}$	$2.740 \times 10^{-4}$	68.6	$3.822 \times 10^{-4}$	95.7
$19.94 \times 10^{-4}$	$4.12 \times 10^{-2}$	$1.424 \times 10^{-4}$	71.3	$1.990 \times 10^{-4}$	99.5
$9.97 \times 10^{-4}$	$3.16 \times 10^{-2}$	$7.319 \times 10^{-5}$	73.1	$1.025 \times 10^{-4}$	102.3
$4.98 \times 10^{-4}$	$2.23 \times 10^{-2}$	$3.752 \times 10^{-5}$	74.6	$5.244 \times 10^{-5}$	104.3
$2.49 \times 10^{-4}$	$1.58 \times 10^{-2}$	$1.929 \times 10^{-5}$	76.1	$2.704 \times 10^{-5}$	106.7
$1.25 \times 10^{-4}$	$1.12 \times 10^{-2}$	$9.806 \times 10^{-6}$	76.1	$1.365 \times 10^{-5}$	105.9
0		$3.297 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 79.1$	$4.486 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 111$

$\Lambda^*$ Equivalent conductance, corrected for conductance of pure solvent





TABLE 10

SPECIFIC CONDUCTANCE ( $\lambda$ ) AND EQUIVALENT CONDUCTANCE ( $\Lambda$ )  
OF LiCl #2 + AlCl<sub>3</sub> #3/AN #3-1 AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$ , molar <sup>1/2</sup>	$\lambda$ (25 C), ohm <sup>-1</sup> cm <sup>-1</sup>	$\Lambda^*$ (25 C), ohm <sup>-1</sup> equ <sup>-1</sup> cm <sup>2</sup>	$\lambda$ (60 C), ohm <sup>-1</sup> cm <sup>-1</sup>	$\Lambda^*$ (60 C), ohm <sup>-1</sup> equ <sup>-1</sup> cm <sup>2</sup>
0.9994**	1.000	$5.087 \times 10^{-2}$	50.9	$6.748 \times 10^{-2}$	67.5
0.1998	0.447	$1.859 \times 10^{-2}$	93.0	$2.279 \times 10^{-2}$	114.0
0.03998	0.200	$4.477 \times 10^{-3}$	112.0	$5.645 \times 10^{-3}$	141.2
0.007998	0.0894	$1.019 \times 10^{-3}$	127.3	$1.288 \times 10^{-3}$	160.9
0.003898	0.0624	$5.320 \times 10^{-4}$	136.4	$6.755 \times 10^{-4}$	173.1
0.001999	0.0470	$2.717 \times 10^{-4}$	135.7	$3.465 \times 10^{-4}$	173.0
0.0009995	0.0316	$1.410 \times 10^{-4}$	140.6	$1.795 \times 10^{-4}$	179.0
0.0004997	0.0224	$7.152 \times 10^{-5}$	142.2	$9.131 \times 10^{-5}$	181.5
0.0002498	0.0158	$3.648 \times 10^{-5}$	144.2	$4.654 \times 10^{-5}$	183.8
0.0001249	0.0112	$1.804 \times 10^{-5}$	140.7	$2.283 \times 10^{-5}$	177.7
0		$4.687 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 148$	$6.335 \times 10^{-7}$	Extrapolated: $\Lambda_0 = 188$

\*\*The initial solution was saturated with LiCl (0.92M); the other solutions were obtained by diluting this solution. The concentration listed refer to AlCl<sub>3</sub> concentration.

$\Lambda^*$ Equivalent conductance, corrected for conductance of pure solvent.

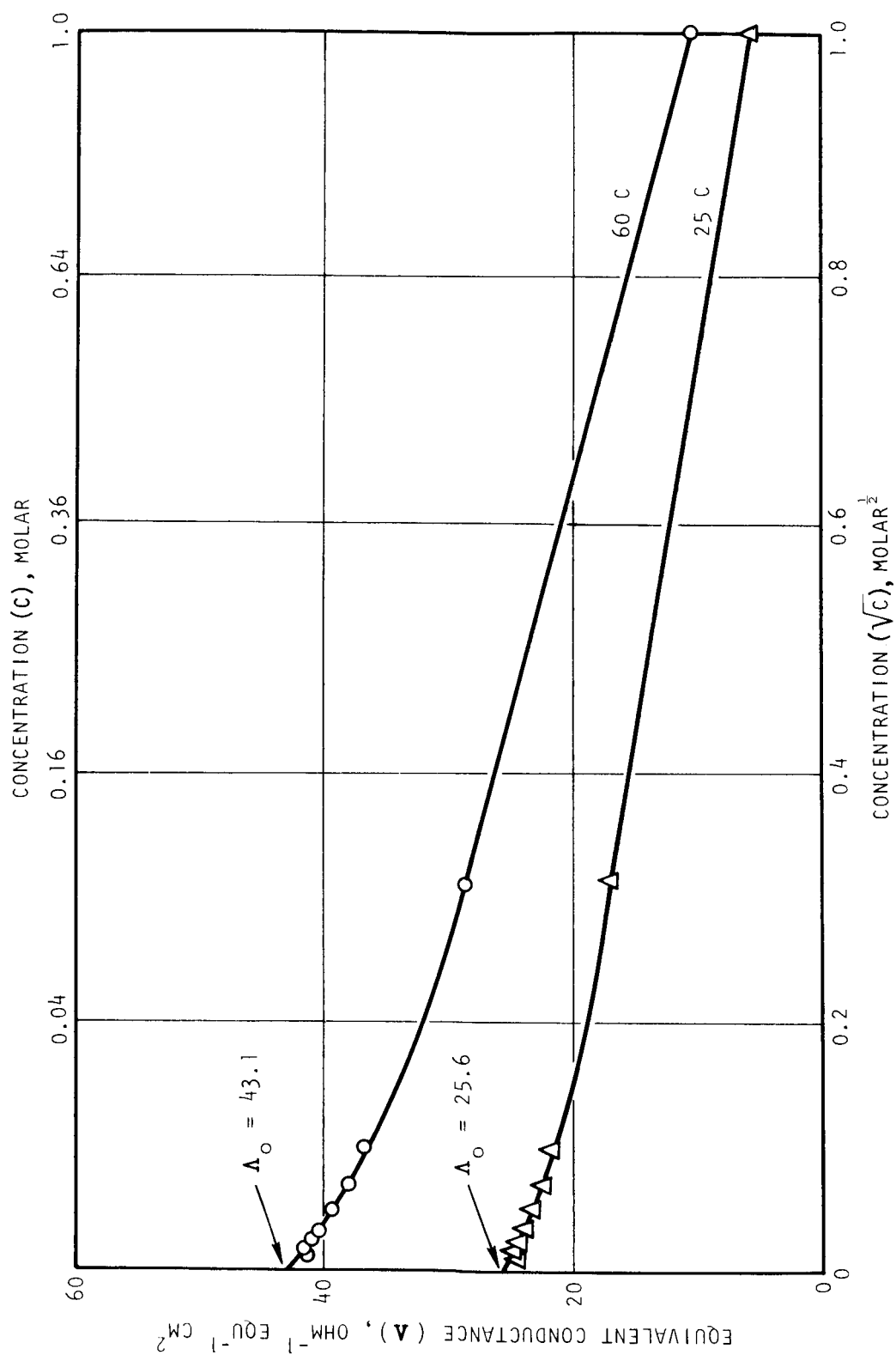


Figure 12. Equivalent Conductance of  $\text{LiClO}_4$  in Propylene Carbonate at 25 and 60 C

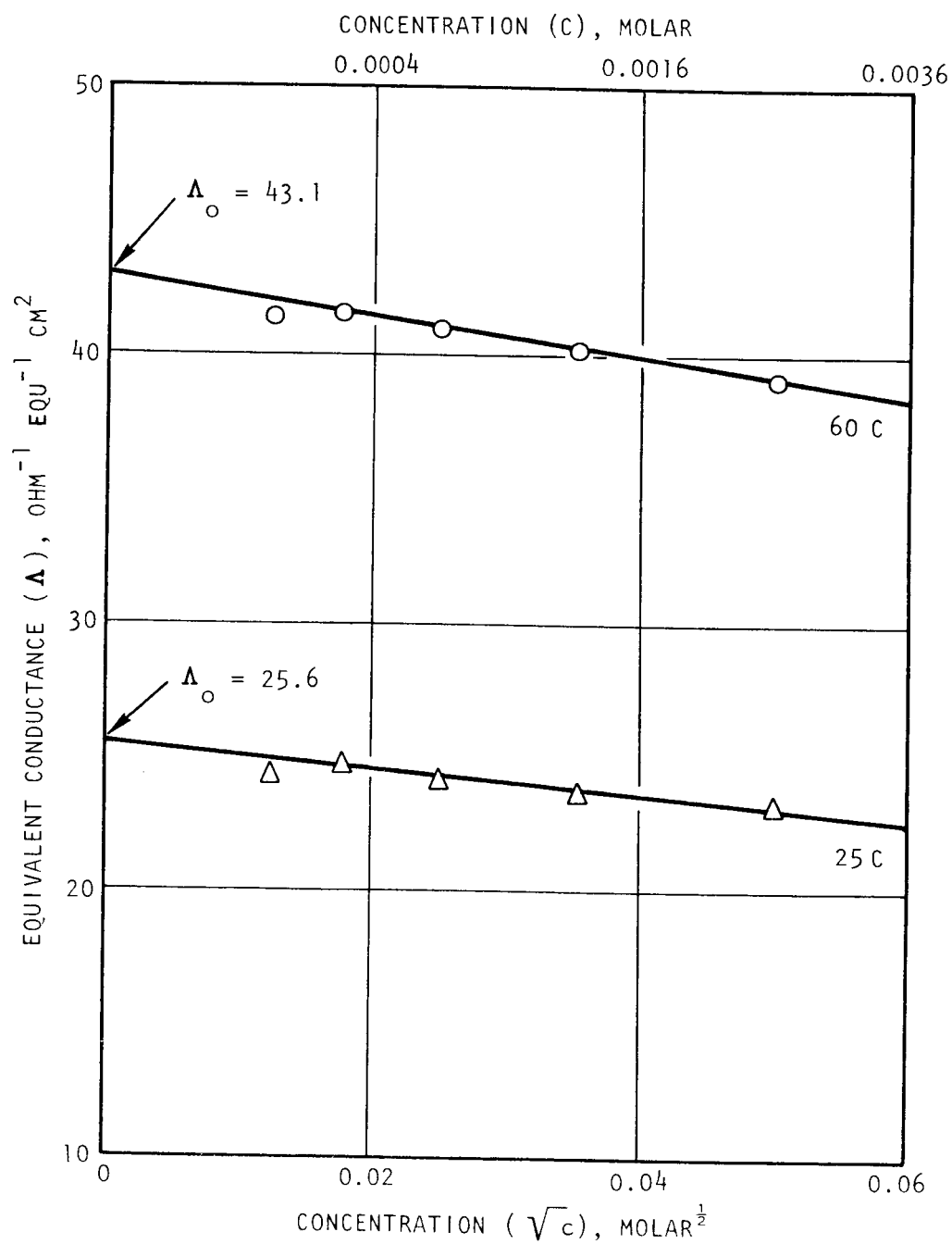


Figure 13. Equivalent Conductance of  $\text{LiClO}_4$  in Propylene Carbonate at 25 and 60 C.

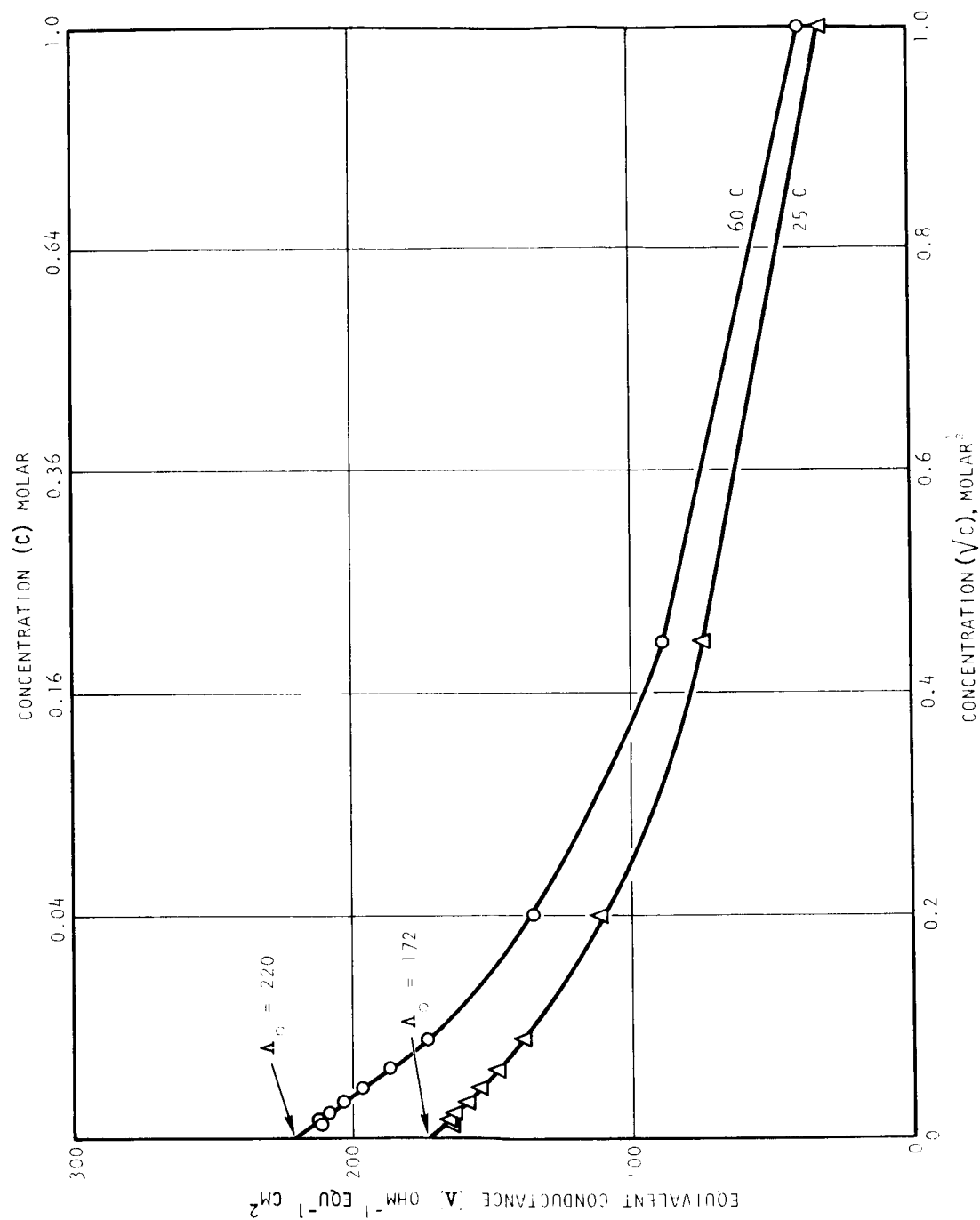


Figure 14. Equivalent Conductance of  $\text{LiClO}_4$  in Acetonitrile at 25 and 60 C

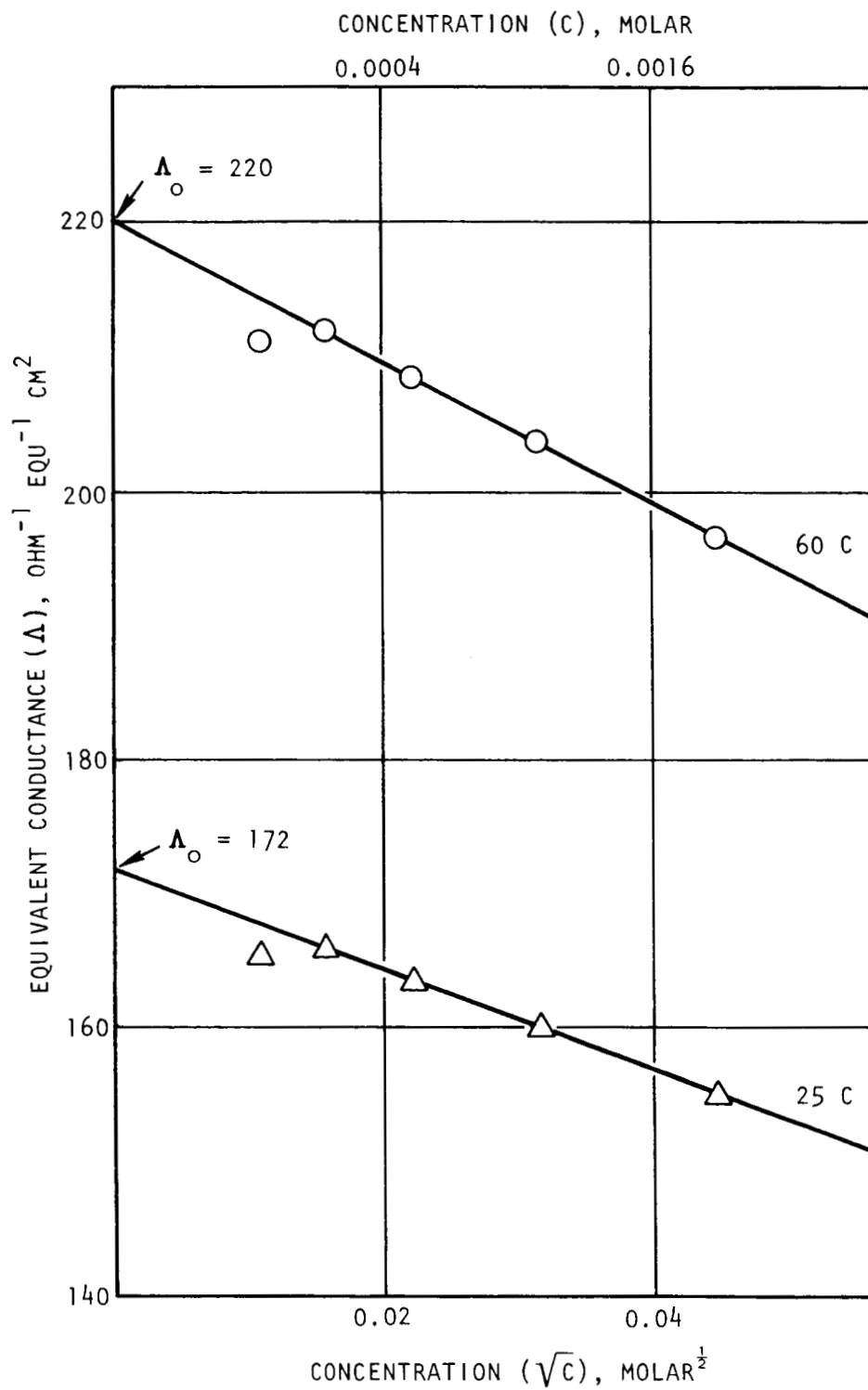


Figure 15. Equivalent Conductance of  $\text{LiClO}_4$  in Acetonitrile at 25 and 60 C.

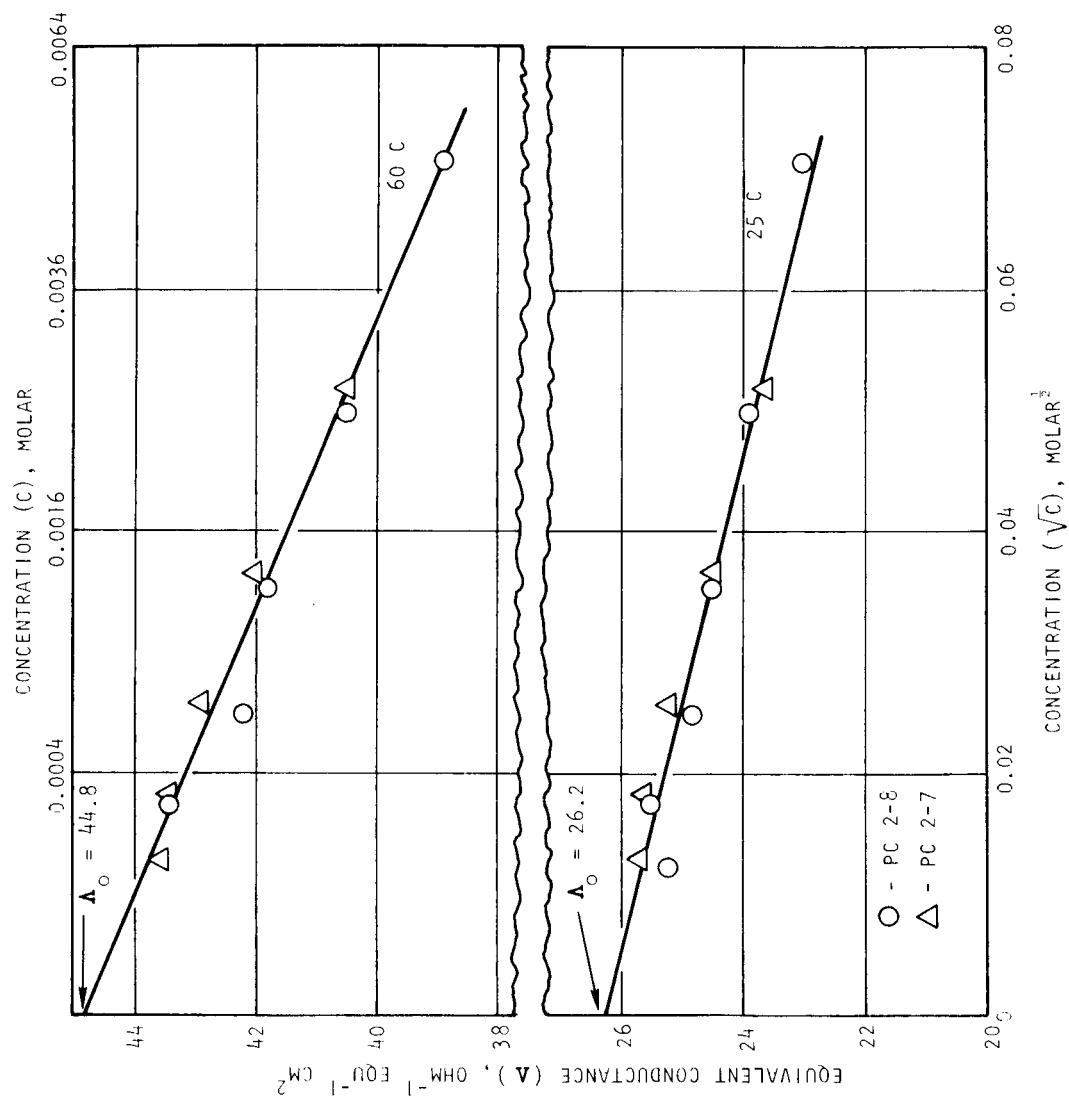


Figure 16. Equivalent Conductance of LiBr in Propylene Carbonate at 25 and 60 C

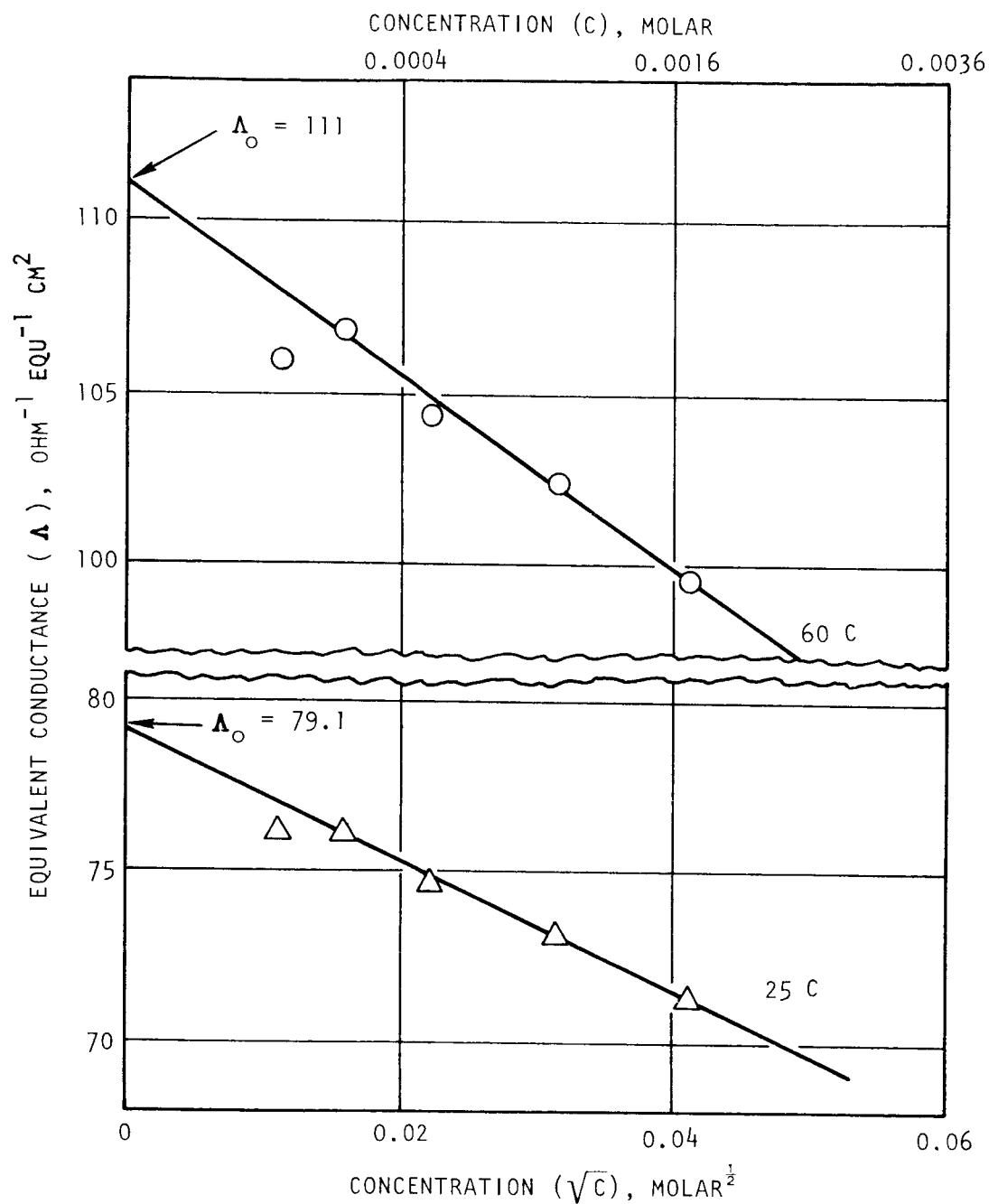


Figure 17. Equivalent Conductance of LiBr in Dimethyl Formamide at 25 and 60C

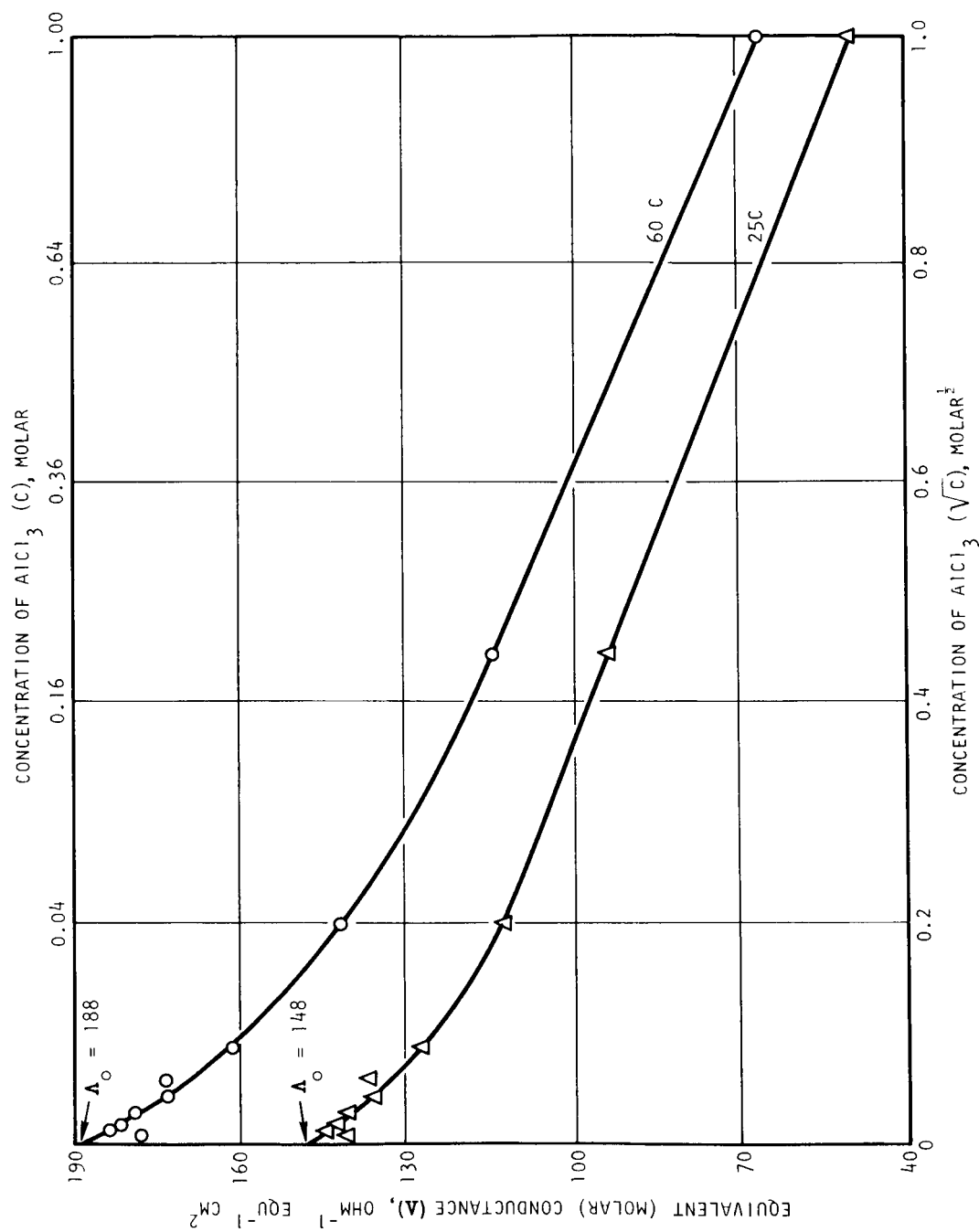


Figure 18. Equivalent (Molar) Conductance of  $\text{LiCl} + \text{AlCl}_3$  in Acetonitrile at 25 and 60 C





### Measurement of Transference Numbers by the Hittorf Method

The cell and the procedure used in these experiments were described previously (Ref. 3).

The transference number of the  $\text{Li}^+$  ion was determined in 1 M  $\text{LiClO}_4/\text{PC}$  and 1 M  $\text{LiClO}_4/\text{DMF}$ . The experimental data are summarized in Table 11. The constant current applied was 16 milliamperes. Silver anodes and nickel cathodes were used. From the decrease of the lithium concentration in the anolyte, a transference number of  $t_+ = 0.19 \pm 0.08$  was obtained for  $\text{LiClO}_4/\text{PC}$ ; the catholyte was not examined because of the uncertainty of the coulombic efficiency of the lithium deposition. This efficiency was determined in the case of 1 M  $\text{LiClO}_4/\text{DMF}$  by determining the amount of lithium on the nickel substrate. The observed decrease of the lithium content of the catholyte was adjusted accordingly. A transference number for the  $\text{Li}^+$  ion of  $t_+ = 0.22$  was calculated from anolyte data and  $t_+ = 0.27$  from catholyte data; the mean value is  $t_+ = 0.25$  with an estimated accuracy of  $\pm 0.04$ . This compares with a value of 0.32 calculated from conductance data at infinite dilution (Ref. 11). The transference number for the lithium ion is considerably lower than the one for the perchlorate ion, both in 1 M  $\text{LiClO}_4/\text{DMF}$  and in 1 M  $\text{LiClO}_4/\text{PC}$ . This is explained by a high degree of solvation of the  $\text{Li}^+$  ion and is in line with previously reported data for  $\text{LiCl}/\text{DMF}$  (Ref. 2) as well as data in aqueous systems.

Hittorf measurements were made with an electrolyte containing  $\text{LiCl}$  and  $\text{AlCl}_3$  in DMF, and the results are summarized in Table 12. A decrease of the aluminum concentration in the anolyte was observed, and the aluminum content in the catholyte increased. This indicates the presence of a positively charged aluminum species. However, the concentration changes



TABLE 11

HITTORF EXPERIMENTS WITH ELECTROLYTES CONTAINING  $\text{LiClO}_4$ 

Solute	Solvent	Total Charge, coulombs	Loss of Li in Anolyte, moles	$t_+$ (From Anolyte Data)	Adjusted Loss of Li in Catholyte, moles	$t_-$ (From Catholyte Data)
1 M $\text{LiClO}_4$ #2	PC #2-7	386	$7.5 \times 10^{-4}$ *	0.19		
1 M $\text{LiClO}_4$ #2	DMF #3-4	434	$1.00 \times 10^{-3}$ **	0.22	$3.27 \times 10^{-3}$	0.73

\*Determined concentration of anolyte at conclusion of experiment: 0.975 M

\*\*Determined concentration of anolyte at conclusion of experiment: 0.97 M



observed were small and not too far beyond the detection limit of the analysis method (atomic absorption) even after the LiCl content of the original solution was dropped from 1 M to 0.5 M. This may indicate either a slowly migrating aluminum species or the presence of more than one aluminum species, a second one being negatively charged or neutral.

TABLE 12

HITTORF EXPERIMENT WITH AN ELECTROLYTE CONTAINING  
LiCl AND  $\text{AlCl}_3$  IN DMF

Run No.	Solutes	Solvent	Total Charge, coulombs	Change of Aluminum Content in Anolyte	Change of Aluminum Content in Catholyte
1	1 M LiCl #2 +0.05 M $\text{AlCl}_3$ #3	DMF #3-3 (50 percent) DMF #3-4 (50 percent)	345	Not determined	$+4.5 \times 10^{-5}$ mole** (corresponds to $n \times 4.3$ coulombs)
2	0.5 M LiCl #2 +0.05 M $\text{AlCl}_3$ #3	DMF #3-5	251	$-4.6 \times 10^{-5}$ mole* (corresponds to $n \times 4.4$ coulombs)	$+8.9 \times 10^{-5}$ mole*** (corresponds to $n \times 8.6$ coulombs)

\*Determined concentration of aluminum at conclusion of experiment: 0.0485 M

\*\*Determined concentration of aluminum at conclusion of experiment: 0.0515 M

\*\*\*Determined concentration of aluminum at conclusion of experiment: 0.053 M

The migration of the copper species in electrolytes containing  $\text{CuCl}_2$  and  $\text{LiClO}_4$  was studied in propylene carbonate and dimethyl formamide. As shown in Table 13, a slight increase in the copper concentration of the



TABLE 13  
HITTORF EXPERIMENTS WITH ELECTROLYTES CONTAINING  $\text{LiClO}_4$  AND  $\text{CuCl}_2$

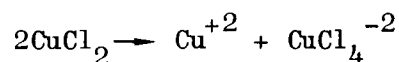
Solutes	Solvent	Total Charge, coulombs	Change of Cu Content in Anolyte	Corresponding Charge, coulombs
$1.1 \times 10^{-3}$ M $\text{CuCl}_2$ #2 + 1 M $\text{LiClO}_4$ #2	PC #2-7 (50 percent) + PC #2-8 (50 percent)	347	$+1.0 \times 10^{-5}$ mole*	$1.0 \times n$
0.1 M $\text{CuCl}_2$ #2 + 1 M $\text{LiClO}_4$ #2	DMF #3-4	288	$+1.85 \times 10^{-4}$ mole**	$17.9 \times n$

\*Determined concentration of Cu at conclusion of experiment:  $1.4 \times 10^{-3}$  M

\*\*Including copper deposited on silver anode; determined concentration of Cu at conclusion of experiment: 0.1025 M



anolyte was observed for 1 M  $\text{LiClO}_4$  + 0.0011 M  $\text{CuCl}_2$ /PC. A more complex situation was encountered in DMF because the copper chloride reacted with the silver anode, as had been observed previously in  $\text{CuCl}_2$  +  $\text{LiCl}$ /DMF (Ref. 3); the amount of copper deposited on the silver anode was determined by analysis and was included in the value of the amount of copper accumulated in the anode compartment. The presence of negatively charged copper species is revealed by these experiments. It is not readily seen what species other than  $\text{CuCl}_3^-$  or  $\text{CuCl}_4^{2-}$  could form because  $\text{ClO}_4^-$  is not expected to complex. It is probable that a positively charged copper species exists besides these negative ions. The copper species might form according to



It is generally true that the concentration changes occurring during these experiments were relatively small. Small errors in the analytical data cause relatively large errors in the computed transference numbers. There exists another factor which further limits the accuracy of the results. The cation and/or anion can be heavily solvated and carry along a number of solvent molecules when migrating in an electric field. An unbalanced transport of solvent may result if cation and anion are solvated to a different extent. The lithium ion, for example, is more heavily solvated than the chloride or the perchlorate ion, as demonstrated by a low transference number. By assuming 6 solvated solvent molecules per lithium ion and none for the anion, the surplus of solvent molecules moving into the cathode compartment can be estimated; for a transference number of 0.3 and a total number of 320 coulombs, it amounts to 0.006 moles. Thirty milliliters of catholyte contain 0.387 mole of DMF, or 0.352 mole of PC, respectively. The resulting dilution effect would amount in this case to nearly 2 percent. In some cases, this would indeed be in the order of



magnitude of the observed concentration changes.\* Working with less concentrated solutions would decrease the effect.

### Heats of Solutions

Various calorimeter designs were investigated for measurements of heats of solutions.

The heat effect expected was estimated by calculating the standard partial molar enthalpy change for the solute from solubility data at two temperatures. Neglecting the comparatively small heat of dilution, the integral heat of solution is approximately 200 calories for a 300-milliliter sample of a 0.15 M solution. For direct measurement of the partial molar enthalpy, the corresponding heat would be 20 calories. In the former case, the temperature rise,  $\Delta T$ , is a few tenths of a degree, and in the latter, a few hundredths. The approximate temperature sensitivity required is  $\sim 5 \times 10^{-5}$  C.

Among the calorimeter systems investigated, the Cobble-type (Ref. 12) vacuum calorimeter appears to be most suitable; it has sufficient sensitivity ( $< 10^{-5}$  C), low heat leak rate, and relative ease of changing temperature from 25 to 60 C. The commercially available LKB calorimeter is of this general type, having  $5 \times 10^{-5}$  C temperature sensitivity and provision for evacuation of the space between the reaction vessel and the jacket.

\*The effect can be estimated only roughly as long as the solvation of the ions involved is not known. It is expected to cause  $t_+$  to appear significantly too low (possibly by about 20 percent or more) in the following solutions: 1 M LiCl/DMF, 1 M LiClO<sub>4</sub>/PC, and 1 M LiClO<sub>4</sub>/DMF. The accumulation of aluminum in the catholyte in LiCl + AlCl<sub>3</sub>/DMF would be greater without the effect than actually was observed; correspondingly, the accumulation of copper species in the anolyte would be smaller in LiCl + CuCl<sub>2</sub>/DMF, LiClO<sub>4</sub> + CuCl<sub>2</sub>/PC, and LiClO<sub>4</sub> + CuCl<sub>2</sub>/DMF. The effect, however, should not influence the basic conclusions drawn above.



### Dielectric Constant

For the determination of the low-frequency dielectric constant of the electrolyte solutions, a microwave measurement method (Ref. 13) together with the Cole-Cole extrapolation procedure has been adopted. The equipment to be used includes 10 to 25 GHz microwave setups and a refractometer to obtain the refractive index.

The microwave method is based on measurement of standing wave position and amplitude. The standing wave results from interference of a reference wave and the wave traveling through the sample. For the 10 GHz frequency, an E-H tee is used to split the wave into the reference and sample waves. In the design (Ref. 13), modification of the E-H tee is made so that a part of the reference wave is reflected back in phase with the wave reflected by the sample. This requires installation of a movable slit (iris) into the reference arm. Work is in progress to add the latter.

The equipment for the 10 GHz setup has been assembled except for the cell and iris. The functioning of the standing wave detector and crystal response law was checked out. At 1-microampere crystal current the response was approximately quadratic (i.e., 2.02).



## WORK PLANNED FOR NEXT QUARTER

### PREPARATION OF ELECTROLYTES

Work on this task will continue. Other solutes will be characterized, and the synthesis of pure  $\text{CuF}_2$  will be attempted.

### NMR STRUCTURAL STUDIES

The  $\text{Cl}^{35}$  and  $\text{Li}^7$  resonances will be studied in electrolytes containing  $\text{LiClO}_4$  and  $\text{LiCl}$ , and the  $\text{Al}^{27}$  resonances in solutions containing  $\text{LiCl}$  and  $\text{AlCl}_3$  at intermediate concentrations. The  $\text{H}^1$  spectra in  $\text{LiCl}+\text{AlCl}_3/\text{AN}$  will be studied at low temperature. The  $\text{Cu}^{63}$  resonance will be investigated in  $\text{LiCl}+\text{CuCl}_2/\text{DMF}$ .

### PHYSICAL PROPERTY DETERMINATIONS

Determinations of physical properties will continue. Solubility studies of lithium fluoride and lithium chloride in electrolyte solutions will be emphasized. Conductances of tetrabutylammonium bromide and tetrabutylammonium tetraphenylboride will be measured to establish individual ion mobilities. Diffusion coefficients will be measured by chronopotentiometry and by a direct method.





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13. ABSTRACT		
<p>Studies of aprotic electrolytes based on three solvents, propylene carbonate, dimethyl formamide and acetonitrile, were continued. Only characterized components were used to prepare the electrolyte solutions.</p> <p>Structural studies of electrolytes containing tetramethylammonium hexafluorophosphate, lithium perchlorate, cupric chloride, and aluminum chloride with or without lithium chloride added were performed by nuclear magnetic resonance.</p> <p>The physical property studies included measurements of viscosities, solubilities, conductances, and transference numbers of a number of electrolytes.</p>		

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